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# Burning Waste Chlorinated Hydrocarbons in a Cement Kiln

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# BURNING WASTE CHLORINATED HYDROCARBONS
# IN A CEMENT KILN

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An experimental program was carried out in 1975/76 at the St. Lawrence Cement Co., Mississauga, Ontario in which waste chlorinated hydrocarbons, containing up to about 46 weight percent chlorine, were burned in a rotary cement kiln. Materials burned included mixtures of ethylene dichloride, chlorotoluene and up to approximately 50 percent polychlorinated biphenyls (PCB).

These materials were destroyed in the cement kiln with at least 99.98 percent efficiency in all cases. Emissions of high molecular weight chlorinated hydrocarbons were not detected. Three light chlorinated hydrocarbons, dichloromethane, chloroform and carbon tetrachloride, were found in the emissions in the part per billion or lower range. The quantity of precipitator dust requiring disposal, as well as emissions of particulate matter, increased during the test. A reduction in fossil fuels used while burning chlorinated hydrocarbons was noted.

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## ABSTRACT

An experimental program was carried out in 1975/76 at the St. Lawrence Cement Co., Mississauga, Ontario in which waste chlorinated hydrocarbons, containing up to about 46 weight percent chlorine, were burned in a rotary cement kiln. The chlorinated hydrocarbons were burned in three distinct phases of increasing difficulty of combustion. Materials burned included mixtures of ethylene dichloride, chlorotoluene and up to approximately 50 percent polychlorinated biphenyls (PCB).

These materials were destroyed in the cement kiln with at least 99.98 percent efficiency in all cases. Emissions of high molecular weight chlorinated hydrocarbons were not detected. Three light chlorinated hydrocarbons, dichloromethane, chloroform and carbon tetrachloride, were found in the emissions in the part per billion or lower range. The quantity of precipitator dust requiring disposal, as well as emissions of particulate matter, increased during the test.

The chlorine input from the chlorinated hydrocarbon waste was up to about 0.8 weight percent relative to clinker and this effectively reduced the alkali concentration of the clinker in direct stoichiometric proportion. A reduction in fossil fuels used while burning chlorinated hydrocarbons was noted.

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# EXECUTIVE OUTLINE

Experiments using chlorinated hydrocarbon wastes in the manufacture of cement appear to have transformed a difficult waste disposal problem into a solution which is not only economically and environmentally satisfactory, but has a beneficial effect on the quality of the cement.

Safe disposal of the large volumes of the chlorinated hydrocarbon wastes which are generated in Canada each year is a difficult environmental problem. It is estimated conservatively that Canada generates some 25-30 million pounds annually of these highly toxic and persistent wastes. This figure does not include many toxic compounds such as insecticides and polychlorinated biphenyls (PCB's).

Environmentally safe disposal is difficult and expensive. Disposal on land, or underground, requires special and expensive precautions to prevent leaching into waterways. The favoured method of disposal, incineration with recovery of hydrogen chloride, can be very costly. Without recovery, scrubbing equipment is required to remove hydrogen chloride from the products of combustion to control its emission. This, in turn, usually necessitates a satisfactory disposal method for the scrubber liquid. Valuable fuel must be burned to maintain combustion while incinerating chlorinated hydrocarbon wastes, as extremely high temperatures with long residence times are required for their thermal destruction.

A long high-temperature flame is required in a cement kiln to achieve the desired product quality. During normal operations, the thermal conditions that are necessary effectively consume the toxic materials. The kiln also contains a considerable quantity of lime and thus has an intensive "scrubbing" action.

Recovery and re-use of hydrocarbon wastes is not always felt to be economic. The recycling of solvents is practiced when it is economically and technically feasible. However, this entails the control of segregation, storage, collection and ultimate treatment of the various hydrocarbon streams.

The report strongly urges that combustible liquid wastes, many of which are persistant environmental contaminants, be combined by means of a

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single economical recovery system which would collect and later use the wastes as supplementary fuel for cement manufacture.

The experiments described in this report were monitored by the Department of Fisheries and Environment, the Ontario Ministry of the Environment, the United States Environmental Protection Agency, and the Ontario Research Foundation.

For these experiments, industrial chlorinated hydrocarbon wastes including polychlorinated biphenyls (PCB's) were burned during the commercial manufacture of cement.

This not only utilized the thermal value of the wastes, with a reduction in oil consumption, but the results showed that almost all the toxic wastes were completely destroyed in the kiln. Emissions of toxic materials into the atmosphere were negligible.

Calcium chloride is often used in cement manufacture to reduce the alkali content of the product. The only apparent effects that the experimental burn had on the quality of the cement were the beneficial effects due to the incidental addition of chloride ion.

# SUMMARY

Chlorinated hydrocarbon wastes were burned in a carefully controlled experimental trial as a partial fuel at the St. Lawrence Cement Co., Mississauga, Ontario. The experiment was conducted to determine whether chlorinated hydrocarbon wastes could be burned in a cement kiln without adverse effects on air pollution levels.

The wastes used included a variety of chlorinated hydrocarbons in the series of program phases designed to progress from easily combusted chlorinated hydrocarbons to those which are combusted only with difficulty. The last phase consisted mainly of polychlorinated biphenyl wastes. These materials were processed and formulated from chemical wastes as required for the different phases and supplied by Chemtrol Pollution Services Inc.

Atmospheric emission measurements were made before, during and after the burning of each blend of chlorinated waste. Two methods of emissions sampling were used during each phase, the method normally used for measuring emissions of particulate matter, and a sampling train designed specially for determining emissions of organic material. All samples from both systems were analyzed for unburned chlorinated hydrocarbons. It was concluded that the combustion efficiency was at least 99.986 percent for the chlorinated hydrocarbons. Approximately 50 ppb of volatile low molecular weight compounds were found in the emission samples. There were no detectable quantities of high molecular weight chlorinated compounds in the stack gases.

A mass balance was carried out on chlorine and potassium. This showed that the chlorine input as chlorinated hydrocarbon was completely reacted with the process solids.

The alkali content of the clinker showed a reduction which corresponded exactly with the quantity of chlorine input to the system. This agreement further confirms the data from emission testing and the mass balance.

While burning chlorinated hydrocarbons with approximately 40 percent chlorine, a decrease in oil consumption equivalent to 65 percent of the Btu content of the chlorinated hydrocarbons was obtained.

The only differences in the quality of clinker produced while burning chlorinated hydrocarbons were the beneficial effects which were expected through the reduction in alkali content.

**It was concluded that chlorinated hydrocarbon wastes may be used in cement kilns, replacing other forms of chlorine used for reduction of alkali content. A small proportion of fossil fuel required for cement manufacture is conserved through use of these materials. Burning chlorinated hydrocarbon wastes is considered a valuable means of destroying persistent and toxic forms of pollutants while recovering useful heat values.**

## RECOMMENDATIONS

The experiments have shown that there is virtually no adverse effect on air pollution levels by burning chlorinated hydrocarbon wastes in a cement kiln. These wastes include polychlorinated biphenyls and other materials which are difficult to destroy. When other methods, such as incineration, are used hydrogen chloride and chlorine may be emitted and, if the incinerator operation is poorly controlled, uncombusted material may be released into the environment.

The following recommendations are the outcome of the present report:

(1) Burning chlorinated hydrocarbon wastes in a cement kiln is considered a valuable means of destruction of persistent and toxic materials which are members of this family of compounds. Since flame temperatures and retention times are similar for all cement plants regardless of type of kiln or fuel used, chlorinated hydrocarbons should be destroyed in any cement kiln. The feasibility of doing so in a particular kiln installation can be determined by a technical and economic review.

(2) Due to lack of familiarity with organic chemicals, it is considered essential that instructions on safe handling procedures be given to cement industry personnel.

(3) Since problems such as precipitation, solidification, heat or gas release can arise through mixing incompatible waste materials in storage tank, it is considered advisable to obtain such materials from one reliable source of supply at any given time.

## LIST OF ABBREVIATIONS

| | |
|---|---|
| APCD | Air Pollution Control Directorate (EPS) |
| BLA | Baseline A, designates emission tests before waste burns |
| BLB | Baseline B, designates emission tests after waste burns |
| DCM | Dichloromethane |
| EC | Electron capture (detector) |
| EPA | Environmental Protection Agency (U.S.) |
| EPS | Environmental Protection Service (Fisheries and Environment Canada) |
| FID | Flame ionization detector |
| GC | Gas chromatography |
| MOE | (Ontario) Ministry of the Environment |
| MS | Mass spectrometry |
| ORF | Ontario Research Foundation |
| PCB | Polychlorinated biphenyl |
| SLC | St. Lawrence Cement Co. |
| TRW | TRW Systems Group |
| T1, T2, T3 | Test one, Test two, Test three |
| WBA | Waste Burn A (chlorinated aliphatics) |
| WBB | Waste Burn B (WBA plus chlorinated aromatics and alicyclics) |
| WBC | Waste Burn C (WBB plus polychlorinated biphenyls) |
| XRF | X-ray fluorescence |

## 1 INTRODUCTION

In Canada each year an estimated 25-30 million pounds of chlorinated hydrocarbon wastes require disposal or destruction, 17-20 million pounds being generated in Ontario [1]. These figures are based on 5-6% of annual production and may be conservative. Experience in Europe indicates that 10% of production is a more reliable estimate of waste material.

There are waste streams from plants manufacturing, processing, or using chlorinated hydrocarbons which must be disposed of, the method of disposal frequently being incineration. Chlorinated wastes other than those directly from chemical plants also present a serious disposal problem. Among these latter chemicals are polychlorinated biphenyls (PCB's) and insecticides which may require disposal.

Many of these wastes are toxic and persistent, and all pose a serious disposal problem. Among the methods presently used are incineration and land disposal. Incineration with recovery of hydrogen chloride can be costly. Without recovery, combustion gases must be scrubbed, thereby generating a liquid waste requiring disposal. Both incineration methods require additional fuel. Deep welling and other similar methods of disposal are environmentally unsound because of the risk of water contamination.

In cement manufacture, the kiln operates at higher temperatures and for longer residence times than those used in incinerators for destruction of these waste materials. It is also common practice in the cement industry to add chlorides to the kiln to reduce the alkali concentration of the final product. Use of chlorinated hydrocarbon wastes in a cement kiln would provide useful recovery of chlorine and energy and, at the same time, solve a serious disposal problem.

The present research program was carried out to determine whether waste chlorinated hydrocarbons can be burned in a rotary cement kiln without causing adverse air pollution. The approach taken was to analyse stack emissions for uncombusted chlorinated hydrocarbon. A material balance on chlorine was undertaken to confirm the emission findings.

## 2 CEMENT MANUFACTURE

### 2.1 General Principles

While a variety of raw materials may be used in cement manufacture, materials containing calcium, silicon, aluminum and iron without an excess of certain other elements are required. These materials are ground to a fine powder called raw meal, the chemical composition of which is carefully controlled by proper blending of the various materials. Normally, blending is achieved by grinding all the raw materials together (intergrinding). Raw meals required for wet and dry processes are similar except that the raw meal for the wet process is in the form of a slurry containing approximately 35% water, while raw meal for the dry process contains less than 0.5% water.

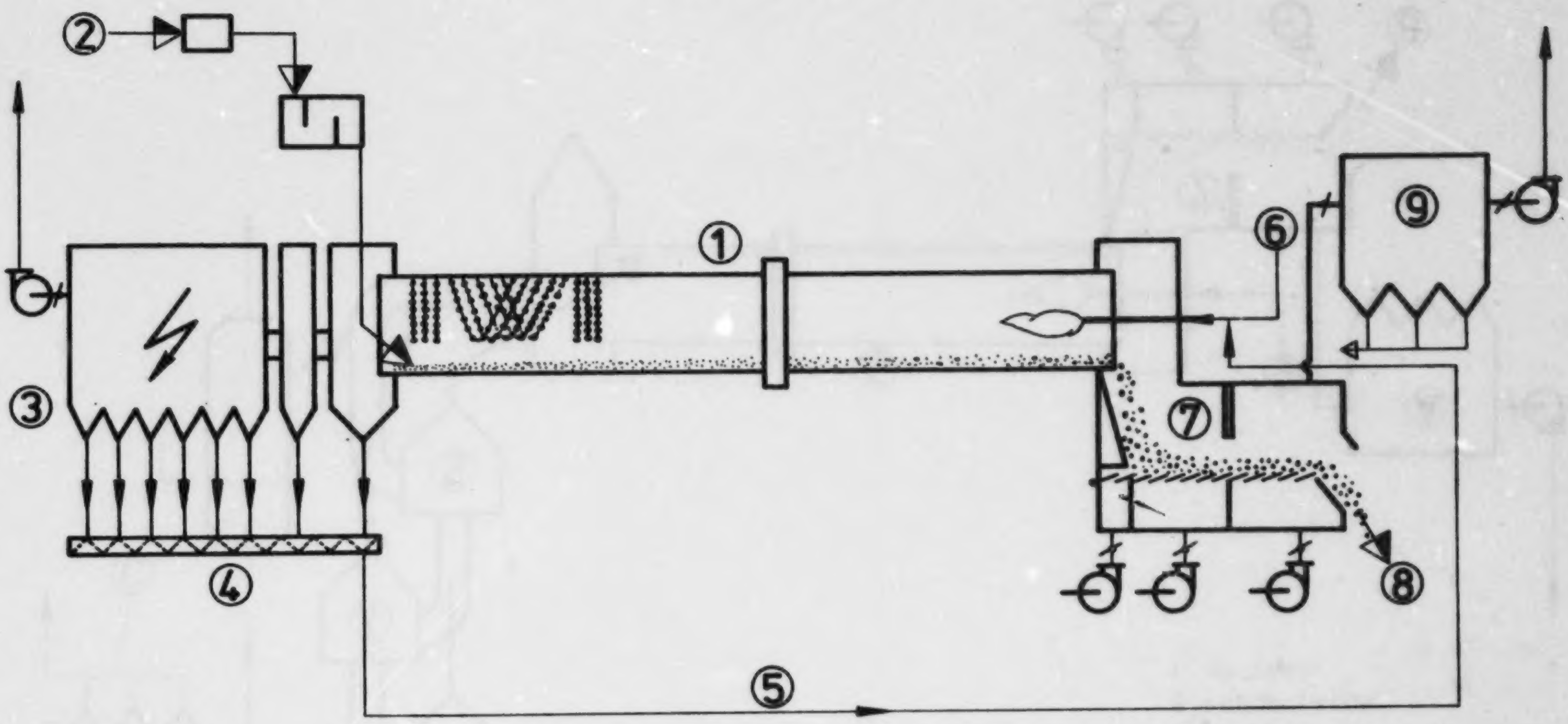
The raw meal is fed into the kiln (see Figures 1 and 2) and is burned in the kiln to produce an intermediate product called clinker.

The kiln slopes towards the burning zone and rotates slowly, causing the raw material to gradually move into the burning zone. Reactions which occur during gradual heating in the kiln are: evaporation of free water, evolution of combined water, evolution of carbon dioxide from carbonates, and combination of lime with silica, alumina and iron to form the desired compounds in the clinker. These reactions require a final material temperature of 1450°C (2650°F). Four main compounds are present in Portland cement clinker:

| Name Of Compound | Chemical Formula | Common Abbreviations Used In The Cement Industry |
|---|---|---|
| Tricalcium Silicate | $3\ CaO{\cdot}SiO_2$ | $C_3S$ |
| Dicalcium Silicate | $2\ CaO{\cdot}SiO_2$ | $C_2S$ |
| Tricalcium Aluminate | $3\ CaO{\cdot}Al_2O_3$ | $C_3A$ |
| Tetracalcium Aluminoferrite | $4\ CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ | $C_4AF$ |

Minor compounds are also formed in clinker, commonly magnesia (MgO), potassium sulfate ($K_2SO_4$) and sodium sulfate ($Na_2SO_4$).

Traces of other elements present in either the raw materials or fuel are also found in clinker. Upon leaving the kiln, the clinker is

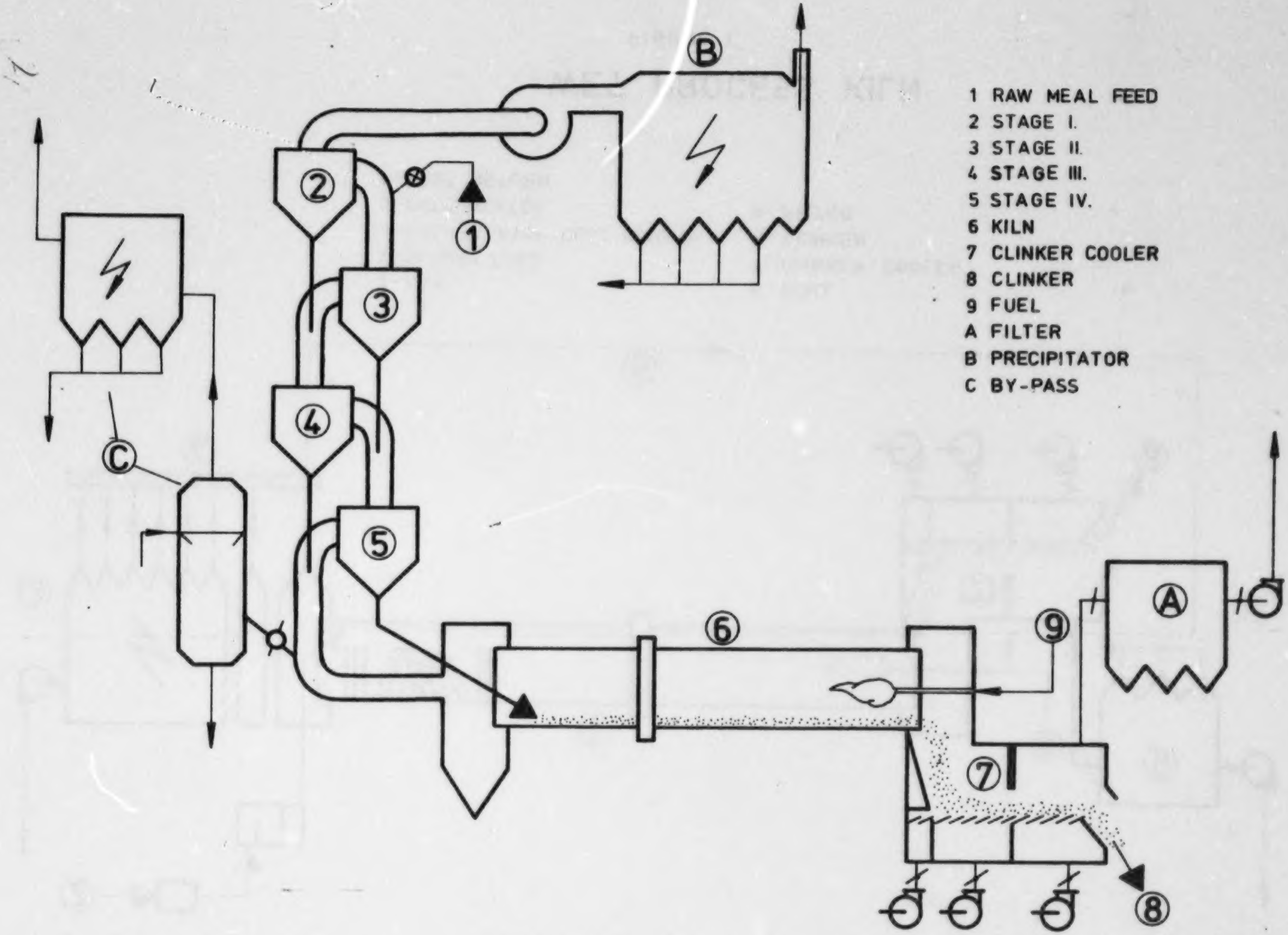


1 - KILN
2 - SLURRY FEED
4 - PRECIPITATOR DUST SCREW
3 - PRECIPITATOR
5 - DUST RETURN

6 - FUEL
7 - CLINKER COOLER
8 - CLINKER
9 - FILTER

WET PROCESS KILN

FIGURE 1.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⑨
Ⓐ
⑦
⑧
1 RAW MEAL FEED
2 STAGE I.
3 STAGE II.
4 STAGE III.
5 STAGE IV.
6 KILN
7 CLINKER COOLER
8 CLINKER
9 FUEL
A FILTER
B PRECIPITATOR
C BY-PASS

DRY PROCESS KILN

FIGURE 2.

rapidly cooled to avoid undesirable crystal forms of the above compounds. After cooling, the clinker is ground and blended, normally by intergrinding, with gypsum to a fine powder. The final product, called Portland cement, is the basic ingredient of concrete.

In the burning process, considerable $CO_2$ is driven from the raw meal. Any elements not driven off are increased in the clinker in proportion to the quantity of $CO_2$ evolved. Throughout most of this report, the analyses have been reported on a natural basis, i.e. reported results are actual concentrations present in samples as received. In some cases, results have been reported on an ignited basis, i.e. on $CO_2$ free basis, and have been indicated as such in the report.

## 2.2 Effect of Alkalies

In cement manufacture, reference to alkalies implies potassium and sodium oxide ($K_2O$ and $Na_2O$). Both alkalies are frequently combined and reported as equivalent $Na_2O$ for purposes of specification. The raw materials at St. Lawrence Cement are such that $Na_2O$ is low and practically constant (see Table A.10). For this reason, only potassium oxide ($K_2O$) is considered in detail in this report.

The effect of alkalies on cement quality has been well documented [2, 3, 4]. While some alkali may be desirable for early strength development [3], an excess can be problematic. The most extensively reported of these problems is the alkali-aggregate reaction [5, 6]. Certain glassy silicates and some dolomites react slowly with alkalies and cause expansion and disruption of concrete. It has been found by experience that cement containing less than 0.60% total alkalies reported as $Na_2O$ performs satisfactorily with such aggregates. This specification is imposed with sufficient frequency in the United States that it is found as an optional specification under ASTM C-150 [7]. Strength attained and setting characteristics are also related to the alkali concentration of the cement [3, 8].

It is common practice in the cement industry to add chlorides such as calcium chloride or waste hydrochloric acid to the raw meal to reduce alkalies [9, 10]. Alkalies are normally present as sulphates which at kiln operating temperatures are not readily volatilized, but are retained in the clinker. Alkali chlorides are volatile at normal kiln operating temperatures. These are evolved from the material in the kiln and carried in the gas stream to the precipitator. The high alkali dust from the precipitator can then be discarded.

### 2.3 The St. Lawrence Cement Co.

The St. Lawrence Cement Co., Mississauga Plant, has a nominal production capacity of 1,750,000 short tons per year. The company operates two wet processes and one dry process suspension preheater kiln. General information on the company and the plant has been published in two articles [11, 12].

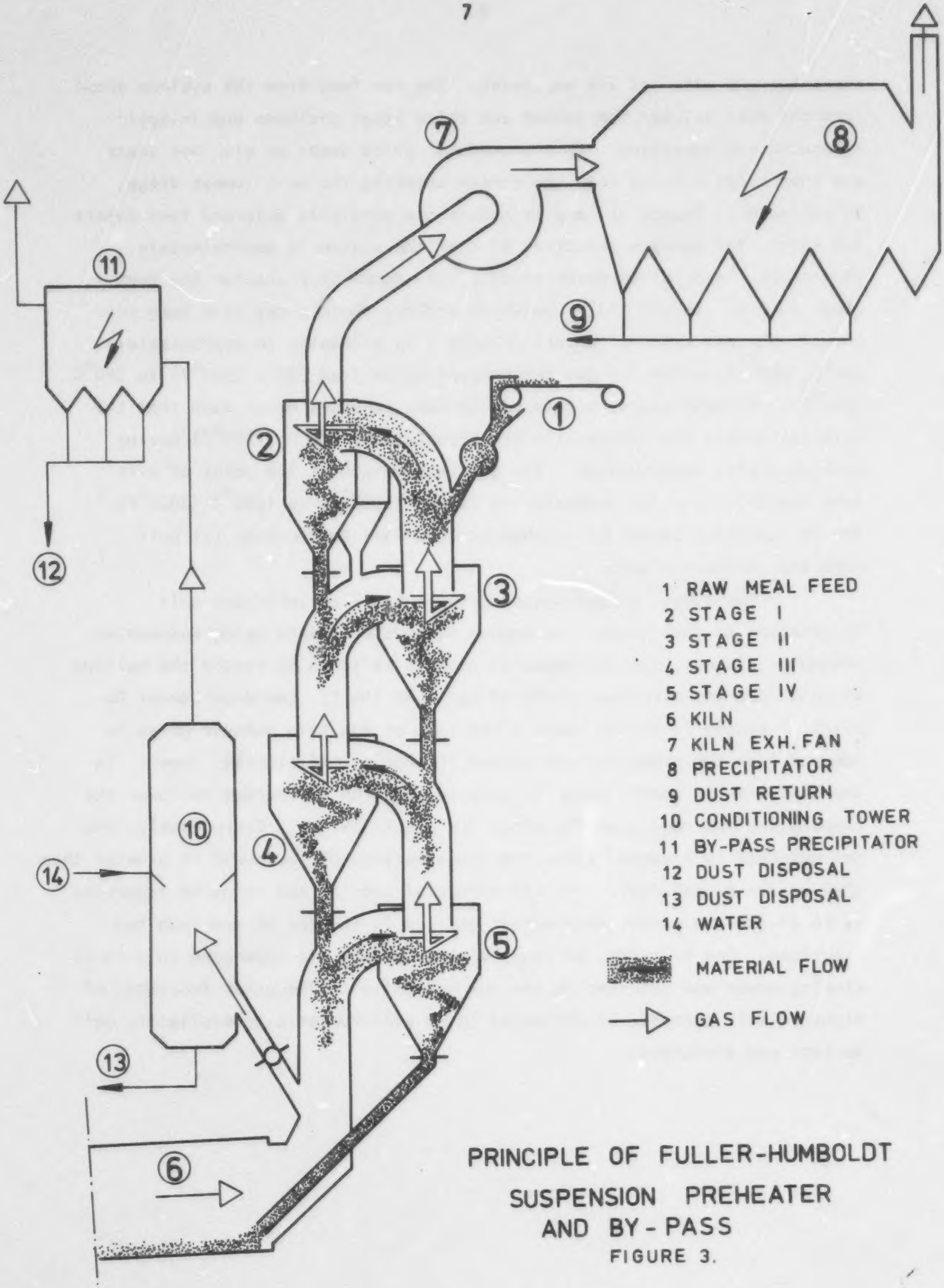
### 2.3.1 Relevant unit processes - wet process kiln

Each of the two wet process kilns are dumbell-shaped Allis Chalmers kilns 402' long with a diameter of 11'6", having nominal capacity of 1050 short tons per day (see Figure 1). The chain system in the drying zone has 57 tons of loose hung carbon steel chains with a radiation curtain at the front (flame end) of stainless steel chains. The chain system extends through 87' of kiln length. The slurry feed system is a bucket wheel conveyor with a variable speed drive taking slurry from a constant level box. Gases from each kiln (maximum capacity 150,000 CFM at 450°F) pass through a six-section electrostatic precipitator. Gases from the precipitators are exhausted via a common stack 554' in height with 13' exit inside diameter. No. 6 fuel oil is burned in a single burner at the centre of the burner pipe. For the test, chlorinated hydrocarbons were fed just above and to one side of centre using different size nozzles for proper atomization at different flow rates. A detailed description of the chlorinated hydrocarbon system is given in Appendix E.

### 2.3.2 Relevant unit processes - suspension preheater kiln

The kiln (Figure 2) is a 17' x 276' Traylor unit normally fired through three nozzles with No. 6 fuel oil. For the test, chlorinated hydrocarbons were injected via a nozzle at the centre of the triangle formed by the three oil nozzles.

The suspension preheater (Figure 3) consists of a system of cyclones through which hot exit gases from the kiln are drawn by a fan. The raw meal passes through the system in counterflow to the gas. Kiln feed is introduced into the duct between the first and second stage cyclones. It is swept with the hot exhaust gases into the uppermost (Stage I) cyclones

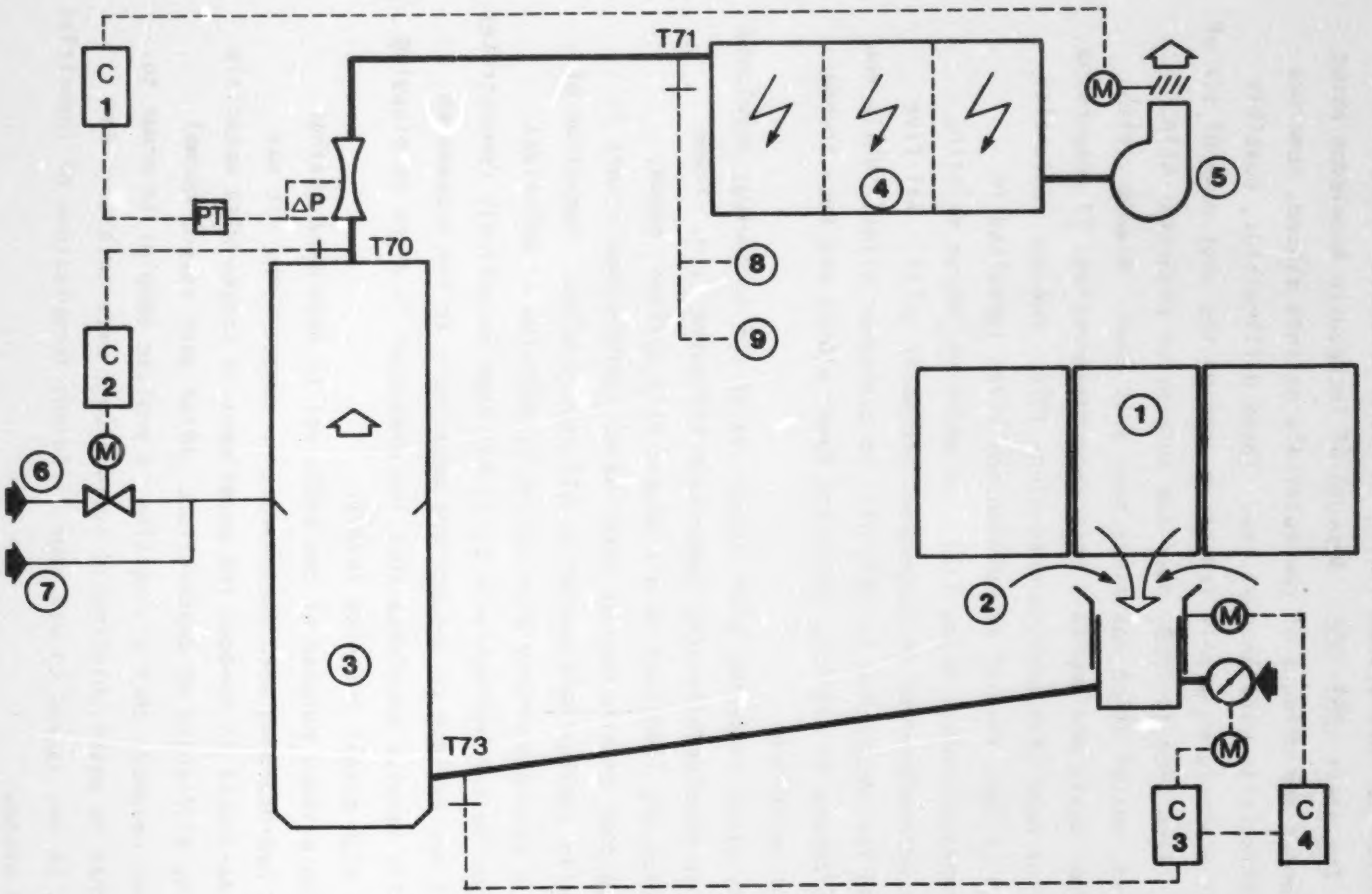

1
2
3
4
5
6
7
8
9
10
11
12
13
14
1 RAW MEAL FEED
2 STAGE I
3 STAGE II
4 STAGE III
5 STAGE IV
6 KILN
7 KILN EXH. FAN
8 PRECIPITATOR
9 DUST RETURN
10 CONDITIONING TOWER
11 BY-PASS PRECIPITATOR
12 DUST DISPOSAL
13 DUST DISPOSAL
14 WATER
MATERIAL FLOW
GAS FLOW

PRINCIPLE OF FULLER-HUMBOLDT SUSPENSION PREHEATER AND BY-PASS

FIGURE 3.

where gas and material are separated. The raw feed from the cyclone drops into the duct between the second and third stage cyclones and is again suspended and separated. This procedure, being swept up with hot gases and then being dropped into the stream entering the next lowest stage, is repeated in Stages III and IV before the partially calcined feed enters the kiln. The average retention time of the system is approximately 30 seconds. A detailed description of the Humboldt preheater has been given by G.A. Schroth [13] from which article these notes have been prepared. The raw material entering Stage I is preheated to approximately 300°C (600°F), while the gas temperature drops from 530°C (990°F) to 340°C (650°F). At each stage, corresponding heat exhanges occur such that the material enters the rotary kiln at approximately 800°C (1475°F) having been partially decarbonated. The gas temperature at the point of exit from the kiln into the preheater is 1040°C (1900°F) to 1090°C (2000°F). The St. Lawrence Cement Co. preheater is a dual Fuller-Humboldt unit with four stages in each.

The alkali bypass system (Figure 4) is an important unit in relation to this study. In common with other plants using suspension preheater systems, special measures have to be taken to reduce the buildup of chlorides and alkalies in the system. At the St. Lawrence Cement Co. plant, a system is in use where a fraction of the kiln exhaust gases is removed from the preheater and passed through a conditioning tower. In the conditioning tower, water is sprayed into the gas stream to lower the temperature and condition the gases for precipitation. Concurrently, the gas velocity is reduced, since the cross section of the tower is greater than that of the bypass duct. The net effect of cooling and velocity reduction is to divide the particulate matter carried in the gas stream into two fractions. One fraction, of lower alkali content, is separated in a conditioning tower and returned to the raw meal silos. The other fraction, of higher alkali content, is collected in an electrostatic precipitator, peletized and discarded.


C 1
PT
ΔP
T70
T71
C 2
M
6
7
3
4
5
M
8
9
1
2
M
M
T73
C 3
C 4

1 PREHEATER TOWER BY-PASS HOOD
2 QUENCH AIR
3 CONDITIONING TOWER
4 PRECIPITATOR
5 EXHAUST FAN
6 WATER
7 AIR
8 650°F CAT OFF CONTROL
9 AIR QUENCH NOZZLE CONTROL (450°F)
C CONTROLLER
PT PRESSURE TRANSMITTER
M MODULATOR

ALKALI BY-PASS
FIGURE 4

## 3 CONSIDERATIONS AT THE PROGRAM PLANNING STAGE

The history of suspension preheater kilns in the United States indicates a trend to this system [14]. Thirteen preheater kilns were installed in the years 1953-1955. Because of inadequate knowledge about the basic process and effects of raw materials on this system, numerous operating difficulties were encountered. These difficulties, possibly combined with emphasis on alkali reduction, caused the shut down of six of these units. From 1956 to 1969, only two suspension preheater kilns were installed, one of which has since been shut down. However, with increasing fuel costs and emphasis on energy conservation, 22 suspension preheater kilns have been commissioned since 1970. Another indication of this trend is that five of the eleven new kilns installed in 1975 were preheater-rotary kilns [15]. In addition, three existing rotary kilns were converted to suspension preheater units. All five kilns planned for completion in 1976 will be preheater kilns. While the situation in Canada is similar, there are fewer plants and such trends are difficult to follow.

Any study concerned with future use of the technology developed must take into consideration the suspension preheater kiln. Flame characteristics are identical in all cement kiln systems, hence, demonstration that destruction of chlorinated hydrocarbons occurs in one cement kiln implies destruction in all cement kilns. Reduction of alkalies in a straight rotary kiln system by addition of chlorides (calcium chloride and hydrochloric acid) has been extensively demonstrated.

It was decided to conduct the experiment in the suspension preheater kiln despite knowledge that the preheater is prone to plugging problems at high alkali chloride levels.

The primary purpose of the study was to determine whether chlorinated hydrocarbons were destroyed in a cement kiln. It was considered desirable to conduct the experiment in stages with materials of increasing difficulty of destruction. After each stage, normal operation was resumed, thus giving time to analyze samples in order to determine that no waste chlorinated hydrocarbons were emitted. For this study, it was agreed to use four different formulations of industrial chlorinated wastes:

1) aliphatics;
2) aromatics;
3) aliphatics plus aromatics and alicyclics; and,
4) aliphatics, aromatics, alicyclics and large complex molecules such as polychlorinated biphyenyls (PCB's).

Generally these are filtered, processed and blended to obtain specific formulations for control of energy value, chlorine content and viscosity.

## 4 TRIAL ON THE SUSPENSION PREHEATER KILN

The first phase of the trial was done in the suspension preheater kiln to determine whether alkali reduction could be accomplished on this unit by burning of chlorinated hydrocarbons. Reduction of alkalies by addition of chloride is achieved by increasing the amount of alkali volatilization. Alkali carbonates and chlorides are almost entirely volatilized at the normal operating temperature of the kiln. Alkali sulphates and alkalies which are complexed in the calcium silicate and aluminate structures are preferentially retained in the clinker.

The addition of chloride ion causes formation of the easily volatilized alkali chloride. Intimate mixing of hot kiln gases and countercurrent cooler raw meal causes alkali chlorides to condense on the raw meal thereby being returned to the kiln. Alkali chlorides are trapped between the burning zone of the kiln (volatilization) and the bottom stage of the preheater (condensation), causing increasing concentrations in the gas stream. At high concentrations of alkali chlorides, sufficient quantities condense in Stages III and IV of the preheater to cause plugging of this system. To alleviate this situation, the bypass is used to withdraw a fraction of the gases leaving the rotary kiln and with these gases a fraction of the alkali chlorides. As greater quantities of alkali chloride are volatilized in the kiln, high withdrawal rates through the bypass are required.

Samples of the raw meal entering the kiln from the preheater can be taken to monitor the alkali chloride concentration. Prior to the burn, it was estimated that equilibrium alkali chloride concentration at this point would be reached in approximately two hours.

Gases exhausted via the bypass have a temperature of approximately 1000°C (1830°F). To cool these gases, they are mixed initially with ambient air, then passed through a conditioning tower in which water spray is used for further cooling and conditioning of the gases. In the conditioning tower, the coarser fraction of the dust, which has the lower alkali concentration, settles to the bottom of the conditioning tower and is returned to the process. The finer fraction, which has the higher alkali concentration, is carried with the gas stream to the bypass precipitator. Dust collected from this precipitator is discarded.

Initially, attempts to operate the bypass at the level required to compensate for addition of chlorides resulted in high emission rates of particulate matter. Weighings of materials showed that 50-60 tons per day of dust were collected in the precipitator (normally 6-10 tons per day), while 4 tons per day settled in the conditioning tower (normally 20 tons per day). The reversal of solids fraction removed in the two units and the larger amount of material carried forward to the electrostatic precipitator was attributed to the increased quantity of ambient air used for cooling the bypass stream. This increased gas flow gave higher velocities in the conditioning tower, lowered its settling efficiency and resulted in particulate entrainment in the gas stream.

The burning of chlorinated aliphatic material was begun on June 3, 1975 with a mixture having a specific gravity of approximately 1.2 and a chlorine content of about 55% w/w.

On June 5, the bypass duct between the kiln and the conditioning tower was plugged. The trial was suspended while the duct was cleaned. A second attempt was begun on June 10 using the same parameters used in the June 3 trial. On June 13, similar buildup again caused the bypass to fail. It was apparent that the addition of chlorides to the suspension preheater kiln could not be done without major portions of the bypass system being rebuilt.

Due to high particulate emissions, plugging of the bypass system and the cost of the equipment changes envisaged to alleviate the short comings, it was decided to continue the trial in one of the two existing wet kilns.

The trial on the dry process kiln did show, however, that chlorinated hydrocarbons were destroyed in this kiln. Chlorinated hydrocarbons used are volatile at temperatures found in Stage IV (980°C), and could not have condensed upon the material. The expected increase in chlorine concentration of Stage IV dusts was confirmed by analyses (Table B.4). Equilibrium concentrations of chloride at Stage IV were obtained in approximately four hours (Appendix B). Some slight alkali reduction was apparent. During the five days on which chlorinated hydrocarbons were burned, the raw meal feed $K_2O$ on ignited basis averaged 1.47%, while the average clinker $K_2O$ was 1.27%. With the same quantity

**of gases being removed by the bypass, but without addition of any chlorinated material, the raw meal feed contained on average 1.44% $K_2O$ and the clinker contained on average 1.29% $K_2O$. While the difference is slight, the duration of the experiment was short.**

**Complete details and analytical results from the experiment on the suspension preheater kiln are given in Appendix B.**

## 5 TRIAL ON THE WET PROCESS KILN

### 5.1 Discussion

The test program for this section of the study was designed to determine if kiln emissions contained any chlorinated organic compounds when chlorinated organic wastes were burned as supplemental fuel to reduce the alkali content of the clinker.

From a knowledge of kiln zone temperatures and gaseous product retention times in the kiln, it was anticipated that combustion of the waste chloride fuel would produce predominantly $CO_2$, $H_2O$, HCl (hydrochloric acid), $Cl^-$ (chloride ion) and a negligible amount of free $Cl_2$ (chlorine gas).

$$H_2O + Cl_2 \rightleftarrows 2HCl + \tfrac{1}{2}O_2$$

$$Kp = \frac{(P_{HCl})^2 \ (P_{O_2})^{\frac{1}{2}}}{(P_{H_2O}) \ (P_{Cl_2})}$$

$$= 15 \text{ at } 1000^\circ C \ (1832^\circ F)$$

$$= 68 \text{ at } 1500^\circ C \ (2732^\circ F)$$

$$= 150 \text{ at } 1500^\circ C \ (3452^\circ F) \ [28].$$

This shows that amount of free chlorine gas decreases with:

a) increase in temperature;
b) increase in water vapor content;
c) decrease in oxygen content; and,
d) decrease or removal of hydrochloric acid.

The hydrochloric acid will react and the chlorine will be retained as alkali chlorides in the process solids. From a knowledge of orthodox incineration systems, the combustion conditions in a cement kiln were expected to provide a very favourable means for the destruction of waste chlorinated hydrocarbons. In order to determine the effect, if any, of burning waste chlorinated organic material on air quality, emissions from the kiln were monitored before, during and after three separate periods of burning the supplemental waste fuels. Prior to each sampling period, emissions were checked for the presence of

HCl and $Cl_2$ with detector tubes at sensitivity limits of 2 ppm and 0.5 ppm, respectively.

A mass balance for chlorine was carried out by analyzing all feed and process samples collected during each waste burn for this element, to confirm the emission data.

Prior to the trial on the wet process kiln, light oil was put into the chlorinated feed system for the purpose of calibrating and testing the proportioning and metering devices. Some light oil remained in the system when chlorinated aliphatic material was received, causing the chloride content to increase as the test progressed. While emissions were tested, chlorinated aliphatic material was burned at different rates while attempting to compensate for the changing chloride content, the rates being equivalent to:

October 28, 1975, 0.31% chlorine relative to clinker;
October 29, 1975, 0.32% chlorine relative to clinker; and
October 30, 1975, 0.63% chlorine relative to clinker.

Due to excessive quantities of chlorine input, a ring was formed, which required a kiln shutdown for its removal. A ring is caused by the buildup of material on the inside of the kiln to such an extent that it restricts the flow of process materials.

Due to production scheduling, the delay caused by the shutdown made it necessary to drop the burning of aromatics alone and immediately progress to the mixture of aromatic and complex molecules. The conductivity of this latter material was too low ($0.3 \times 10^{-6}$ mhos) for the magnetic flow meter to function properly.

Control of flow rates was therefore achieved by measuring the depth of liquid in the tank. While accurate over a long period of time, short term control was difficult because one inch of liquid in the tank is 196 imperial gallons. Variable flow rates were encountered during emission testing, the quantity added each day being:

December 10, 1975, 0.45 to 0.71% chlorine relative to clinker;
December 11, 1975, 0.31 to 0.51% chlorine relative to clinker; and,
December 12, 1975, 0.79% chlorine relative to clinker.

A ring also formed during this burn but broke away after the sampling sequence had been completed, thus avoiding another kiln shutdown. The presence of this ring restricted the burning of the residual quantity of this material (aromatic plus complexes) to intermittent burns.

Due to the above mentioned upset and requirements of the production schedule, it became necessary to add 13,000 gallons of the polychlorinated biphenyl blend to the 12,000 gallons of material remaining in the tank. The resulting mixture contained a significant quantity of solids and also had very low conductivity, thus requiring tank measurements as the method used for flow control.

The problem with solids separation and settling became more severe as the test progressed. This caused burner nozzle restrictions and pluggages which, in turn, caused interruptions and irregularities in waste liquid flows.

For the last day of emission testing, the nozzle was removed completely to permit uninterrupted flow rates of polychlorinated biphenyls. Quantities added during emission tests were:

January 7, 1976, 0.06 to 0.14% chlorine relative to clinker;
January 8, 1976, 0.13 to 0.33% chlorine relative to clinker; and,
January 9, 1976, 0.61% chlorine relative to clinker.

## 5.2 Organic Chloride Waste Burned

The chemical compositions of the three waste materials burned, the labelling used to identify each burn and the time periods during which they were fed to the kiln are given below:

| | | |
|---|---|---|
| Chlorinated aliphatics | WBA | October 23 - November 4/75 |
| WBA plus chlorinated aromatics and alicyclics | WBB | December 5 - December 15/75 |
| WBB plus polychlorinated biphenyls (PCB's) | WBC | January 3 - January 9/76 |

It was anticipated that complete combustion of these materials would occur in the kiln. However, a knowledge of the major constituents of each of the fuels was necessary in order to determine which trace components might be detected in the sampled emissions should incomplete combustion occur. Previous studies on the incineration of waste chlorinated hydrocarbons [16] had shown that trace quantities of low molecular weight compounds such as carbon tetrachloride ($CCl_4$), chloroform ($CHCl_3$), dichloromethane ($CH_2Cl_2$) were detected in the combustion product gases. It was decided, therefore, to analyze collected emission samples for the presence of the major components of each composite waste fraction, and for the low molecular weight organochlorides referred to above.

Samples of the chlorinated wastes were taken from the line between the tank and the kiln. Typical component analyses of the three composite wastes burned during the program are recorded in Tables 1, 2 and 3.

The quantitative values given in the tables are based upon an assumed equal response of all the components to a flame ionization detector (FID). While this assumption is not very accurate, it was considered sufficient to provide the needed compositional data. Identification of components at concentrations greater than one percent was achieved by use of gas chromatography-mass spectrometry (GC-MS). Identification of components at concentrations less than one percent was not routinely performed. Analyses of samples collected on different days during a burn showed some variation in the concentration of individual components. However, the overall chemical composition of the feeds remained the same.

Two of the waste burn sample feeds (WBB and WBC) were also analyzed by the Ontario Ministry of the Environment (MOE), and the TRW Systems Group. The results obtained by these agencies are reported in detail in Appendices F and G, respectively. The TRW Systems Group analyzed composite samples of the daily feeds for both waste burns by GC-MS. The MOE group analysed individual daily samples for both waste burns using GC-FID operating conditions. The chromatographic parameters used by the MOE group to analyse for aromatic and PCB components precluded the identification of aliphatic organochlorine compounds such as $CHCl_3$ and $CCl_4$.

Some variation in the percent composition of the waste burn samples was apparent between the TRW and ORF results, especially with respect to the amounts of aliphatic organochlorine compounds present in waste burn B (WBB). The discrepancies observed are due to the fact that TRW received a composite sample of all daily feeds for each of the

## TABLE 1. COMPOSITION OF ALIPHATICS (WBA)

Sample Feed - October 28, 1975

| Peak # in GC Profile (cf Figure A.6) | Approximate Concentration % | Identification |
|---|---|---|
| 1 | 17.4 | Chloropropane & propene ethylchloride, dichloromethane |
| 2 | 1.4 | |
| 3 | 0.8 | Chlorobutane & butene |
| 4 | 1.5 | |
| 5 | 3.2 | |
| 6 | 16.5 | 1, 2, Dichloroethane |
| 7 | 6.6 | Carbon tetrachloride |
| 8 | 1.0 | |
| 9 | 10.5 | 1, 1, 2-Trichloroethane |
| 10 | 0.7 | |
| 11 | 0.3 | |
| 12 | 1.9 | Dichloropropanes |
| 13 | 1.4 | |
| 14 | 1.4 | |
| 15 | 2.4 | Tetrachloroethylene |
| 16 | 7.3 | Tetrachloroethane |
| 17 | 15.6 | Chlorobenzene |
| 18 | 2.4 | multichlorinated butanes, butenes hexanes, hexenes |
| 19 | 0.2 | |
| 20 | 3.3 | |
| 21 | 0.3 | |
| 22 | 1.1 | |
| 23 | 0.6 | |
| 24 | 0.5 | |
| 25 | 1.6 | |
| 26 | 0.6 | |
| 27 | 0.7 | |

Note: No identification of compounds at concentrations of 1% or less was attempted.

## TABLE 2. COMPOSITION OF AROMATICS PLUS COMPLEX (WBB)

Sample Feed - December 12, 1975

| Peak # in GC Profile (cf Figure A.7) | Approximate Concentration % | Identification |
|---|---|---|
| 1 | 2.0 | Chloropropane |
| 2 | 0.1 | - |
| 3 | 0.1 | - |
| 4 | 1.4 | Chloroform |
| 5 | 1.5 | 1, 2-Dichloroethane |
| 6 | 3.5 | Carbon tetrachloride |
| 7 | 0.4 | - |
| 8 | 1.1 | - |
| 9 | 1.9 | 1, 1, 2-Trichloroethane |
| 10 | 0.2 | - |
| 11 | 0.2 | - |
| 12 | 0.4 | - |
| 13 | 0.6 | - |
| 14 | 0.5 | Chlorobenzene |
| 15 | 0.5 | - |
| 16 | 52.2 | Chlorotoluene |
| 17 | 0.2 | - |
| 18 | 0.1 | - |
| 19 | 0.1 | - |
| 20 | 6.3 | Hexachlorocyclopentadiene |
| 21 | 2.7 | Heptachlorocyclopentene |
| 22 | 0.1 | - |
| 23 | 1.0 | Pentachlorobenzene |
| 24 | 8.5 | Octachlorocyclopentene |
| 25 | 4.4 | Complex associated with Hexachlorocyclopentadiene |
| 26 | 6.9 | |
| 27 | 1.3 | |

Note: No identification of compounds at concentrations of 1% or less was attempted.

## TABLE 3. COMPOSITION OF AROMATICS PLUS PCB's (WBC)

### Sample Feed - January 8, 1976

| Peak # in GC Profile (cf Figure A.8) | Approximate Concentration % | Identification |
|---|---|---|
| 1 | 3.4 | Chloropropane |
| 2 | 0.3 | - |
| 3 | 1.4 | 1, 1,-Dichloroethane |
| 4 | 1.3 | Carbon tetrachloride |
| 5 | 0.5 | - |
| 6 | 0.3 | - |
| 7 | 1.9 | 1, 1, 2-Trichloroethane |
| 8 | 0.1 | - |
| 9 | 1.9 | - |
| 10 | 0.5 | - |
| 11 | 28.5 | Chlorotoluene |
| 12 | < 0.1 | - |
| 13 | < 0.1 | - |
| 14 | 1.8 | Hexachlorocyclopentadiene + complex |
| 15 | 0.9 | |
| 16 | 2.8 | |
| 17 | 0.9 | |
| 18 | 2.2 | Dichlorobiphenyl |
| 19 | 0.3 | |
| 20 | 2.1 | |
| 21 | 0.9 | |
| 22 | 6.7 | Trichlorobiphenyl |
| 23 | 3.4 | |
| 24 | 5.9 | |
| 25 | 1.6 | Tetrachlorobiphenyl |
| 26 | 12.1 | |
| 27 | 5.6 | |
| 28 | 4.0 | |
| 29 | 5.4 | Pentachlorobiphenyl |
| 30 | 2.1 | |
| 31 | 1.6 | |

Note: No identification of compounds at concentrations of 1% or less was attempted.

waste burns, and different chromatographic columns and a different detector system were used by the two laboratories.

Since the study was to evaluate the burning of waste chlorinated materials of variable composition, minor differences between the laboratories' results do not affect the conclusions of the study.

The agreement among all groups was good with respect to the identification of components present in the two waste fuels. The presence of chlorinated aliphatics was observed in both waste fuels. WBB samples were found to consist primarily of chlorinated aromatic compounds, in particular o-chlorotoluene. WBC samples were found to consist of approximately 50% polychlorinated biphenyls (Aroclor 1242) plus the chlorinated aromatics and alicyclics found in WBB samples.

### 5.3 Emissions

Samples of the kiln emissions before (BLA), during (WBA, WBB, WBC), and after (BLB) the burning of waste organic chlorides were taken, using the equipment and methods described in Appendix A. The analytical techniques used to determine if any organic chloride compounds were present in the emissions samples are discussed with respect to both gaseous and particulate emissions.

#### 5.3.1 Free chlorine and hydrogen chloride

Prior to each sampling period, analyses were made for the presence of free chlorine ($Cl_2$) and hydrogen chloride (HCl) in the kiln emissions. An MSA gas sampler and MSA detector tubes were used to determine the concentrations of these pollutants. In no instance, either during baseline or waste burn sampling periods, were $Cl_2$ or HCl detected. The sensitivity limits using this analytical procedure are 0.5 ppm for $Cl_2$ and 2.0 ppm for HCl.

#### 5.3.2 Gaseous organic compounds

Emission samples were collected using two sampling trains. The first, a gaseous sampling train (Appendix H), was designed to collect any volatile low molecular weight organic chlorides, e.g. $CCl_4$, $CHCl_3$, $CH_2Cl_2$, by adsorption on an inert adsorbent. In this study Chromosorb 102 was used. The second, a particulate sampling train (EPA Joy #5), was expected to collect higher molecular weight compounds, including any noncombusted starting materials in the impingers.

Components adsorbed on the sorbent were removed by thermal desorption prior to analysis. All other collected fractions, from both trains, were extracted with organic solvents prior to analysis. These included probe rinse water solubles and insolubles, filters and impinger solutions.

In considering the results obtained in this study it is important to keep in mind the following:

- The collection efficiency of Chromosorb 102 sorbent for low molecular weight chlorinated hydrocarbons was determined to be better than 90%. The collection efficiencies of filters and ice-water in the impingers of a Joy train for organochloride components was not determined.
- The methods of collection, followed by thermal desorption or solvent extraction, were designed to concentrate any organic compounds which may have been present. Such techniques allow detection and identification of compounds at much lower levels than would otherwise be possible. Concentration factors for each type of sample have been calculated for each phase of the burn and are given in Table 4. For the desorbed gas samples, organic compounds from several cubic feet of kiln emission gases were collected on Chromosorb 102 and then desorbed into 500 millilitres. The concentration factors are the ratios of these two volumes. In the case of the solvent extracted samples, molecular weights enter the calculation in the conversion of volume to weight. A complete discussion of these calculations is given in Section A.6.4.

5.3.2.1 Desorbed samples. The concentrations of volatile organic chlorides calculated for the kiln emissions from gas chromatography - electron capture (GC-EC) are recorded in Table 5.

The results reported were averaged for each test series. Dichloromethane (DCM) was tentatively identified as the major component of these desorbed gas samples. Others tentatively identified were $CHCl_3$

## TABLE 4. GAS SAMPLE VOLUMES AND SAMPLE CONCENTRATION FACTORS (Gaseous Sampling Train)

| Test # | Date | Test Duration (mins) | Volume* Sampled scf | Sample Concentration Factors | |
|---|---|---|---|---|---|
| | | | | Desorbed Gas | Solvent** Extracted |
| 1 BLA | Oct. 20 (1975) | 317 | 2.80 | 159 | 510 |
| 2 BLA | Oct. 21 | 281 | 1.86 | 141 | |
| 3 BLA | Oct. 22 | 320 | 2.83 | 160 | |
| 1 WBA | Oct. 28 | 362 | 3.22 | 181 | 500-1100 |
| 2 WBA | Oct. 29 | 286 | 2.53 | 143 | |
| 3 WBA | Oct. 30 | 285 | 2.53 | 143 | |
| 1 WBB | Dec. 10 | 260 | 2.30 | 130 | 600-2000 |
| 2 WBB | Dec. 11 | 317 | 2.80 | 159 | |
| 3 WBB | Dec. 12 | 250 | 2.21 | 125 | |
| 1 WBC | Jan. 7 (1976) | 268 | 2.37 | 134 | 520-1500 |
| 2 WBC | Jan. 8 | 237 | 2.09 | 119 | |
| 3 WBC | Jan. 9 | 228 | 2.02 | 114 | |
| 1 BLB | Jan. 19 | 170 | 1.50 | 85 | 380 |
| 2 BLB | Jan. 20 | 247 | 2.18 | 124 | |
| 3 BLB | Jan. 21 | 240 | 2.12 | 120 | |

*Volume sampled per adsorbent tube.

**These values are based on the lowest and highest molecular weights of compounds found in the waste feeds. Figures given for both baseline series are based upon the molecular weight of dichloromethane (DCM).

TABLE 5. ESTIMATED KILN EMISSION CONCENTRATIONS (GC-EC) FOR SPECIFIC VOLATILE ORGANOCHLORINE COMPOUNDS

| Test Series | Emission Concentrations | | | | | |
|---|---|---|---|---|---|---|
| | Dichloromethane | | Chloroform | | Carbon Tetrachloride | |
| | ppb | μg/m$^3$ | ppb | μg/m$^3$ | ppb | μg/m$^3$ |
| BLA | 4.1 | 14.5 | 0.004 | 0.020 | 0.0004 | 0.0026 |
| WBA | 5.4 | 27.3 | 0.015 | 0.080 | 0.0020 | 0.0128 |
| WBB | 18.0 | 19.1 | 0.038 | 0.190 | 0.0020 | 0.0128 |
| WBC | 7.7 | 102.7 | 0.069 | 0.345 | 0.0060 | 0.0385 |
| BLB | 29.0 | 63.7 | 0.018 | 0.090 | 0.0004 | 0.0160 |

and $CCl_4$. It was found that GC-EC profiles of blank determinations obtained with unused conditioned Chromosorb 102 were variable, and the peaks that were present in the profiles possessed similar retention times to the compounds of interest. Therefore, reported results are higher than actual concentrations in the emission gases. The differing concentrations for DCM quoted in Table 5, especially with respect to BLB versus BLA, WBA or WBB, are probably a result of this background contamination rather than real differences. It was still noted, however, that the maximum concentration calculated as DCM in the kiln emissions was no greater than 30 ppb even with this positive bias from background contamination.

The MOE results confirm the ORF findings with respect to the detection of low molecular weight chlorinated organics in the desorbed gas samples. TRW did not find any trace of these volatile chlorinated organics in their desorbed gas samples. However, TRW did not routinely perform specific analyses for compounds present at concentrations below 0.1 mg/m$^3$.

5.3.2.2 Organic solvent extracted samples. Due to the much higher gas flow rate through the particulate sampling train to maintain an isokinetic sampling rate, the concentration factors for solvent extracted samples for this train were greater than those collected with the gaseous train. Calculated average concentration factors for each test series are given below:

| | |
|---|---|
| BLA | 7,000 |
| WBA | 6,000 - 13,000 |
| WBB | 7,000 - 23,000 |
| WBC | 7,000 - 20,000 |
| BLB | 6,000 |

For the waste burns, the two values given represent the highest and lowest molecular weight species present in the waste chlorinated hydrocarbons. Calculations for the baselines are based on the molecular weight of dichloromethane. Subtraction of background interference based on control blanks (Appendix A.6.3) was performed on solvent extracted samples. Comparison was then made with the appropriate waste feed sample chromatograms. It was concluded that no uncombusted waste fuel components were present in any of the organic solvent extract samples at the detection limits of the analytical procedure used. Representative chromatograms together with discussion are presented in Appendix A.6.5.

TRW performed analyses on portions of all the organic solvent extracts obtained from BLA, WBB, WBC and BLB emission samples. The samples were specifically searched for chlorinated compounds. Also, the Chemistry Division, Air Pollution Control Directorate (APCD), Department of the Environment, Ottawa, Canada carried out analyses on portions of the solvent extracts of WBC emission samples to search for high molecular weight chlorinated hydrocarbons. Detailed reports of the work undertaken by these groups are presented in Appendices G and I, respectively.

The noteworthy result with respect to both reports was that in none of the samples analyzed by either group were any chlorinated organic compounds detected. Their results thus confirm the ORF conclusion that no chlorinated organic residues were detectable in any of the organic solvent extracts of the emission samples collected during the various waste chlorinated hydrocarbon burns.

5.3.2.3 Results obtained by the participating laboratories. In gas chromatographic analyses, program parameters define the conditions used. The choice of detector and column makes the analysis specific to certain

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groups of compounds. Four laboratories analyzed the emissions samples taken during this study.

One of the laboratories, APCD, was requested to search for high molecular weight chlorinated hydrocarbons. The TRW group were not requested to identify low molecular weight chlorinated compounds present at less than 0.1 mg/m$^3$ in the stack gases. TRW did, however, search for PCB's using techniques designed to detect small quantities of these compounds. ORF and MOE were assigned the task of detecting and identifying all possible chlorinated organic species. Analytical design, and hence results, reflect differences in the analyses requested of the different laboratories.

Both ORF and MOE found low molecular weight hydrocarbons, such as dichloromethane, to be present at microgram per cubic meter (μg/m$^3$) levels in the emissions. That TRW detected no such compounds is not contradictory. The levels in the emission gases were less than their required detection limits. Similarly, it was not within the terms of reference for the APCD work to determine these compounds.

Results of the four laboratories can be conveniently summarized. While burning chlorinated hydrocarbons, low molecular weight chlorinated compounds were emitted at levels of a few μg/m$^3$ (Table 5). None of the participating laboratories detected any high molecular weight chlorinated hydrocarbons from either air sampling train. At detection limits of 3 μg/m$^3$ in the stack gases, polychlorinated biphenyls were not found.

5.3.2.4 Estimated minimum combustion efficiencies. The maximum value for total chlorinated hydrocarbon content in the kiln emissions was obtained in test 2 of the WBC series. Ignoring background subtraction for the baseline samples and the interferences from control blanks a maximum value of 40 ppb was determined. If a collection efficiency of 80% is assumed, a maximum level of 50 ppb in the kiln emissions is obtained. Because of the high and uncertain background levels, the estimate is higher than actual levels in the emission gases.

An average molecular weight for each of the three composite feeds can be obtained from a knowledge of the composition of the feed. Using this information, together with the average fuel feed rates to the kiln and average gas volume flow rates in the duct, the maximum chlorinated hydrocarbon content can be determined. These values are presented in Table 6. Minimum combustion efficiencies were then calculated using the estimated maximum value of 50 ppb derived above. These figures in Table 6 are considered very conservative estimates because of the method used to calculate them.

TABLE 6. ESTIMATED MINIMUM COMBUSTION EFFICIENCIES FOR EACH WASTE BURN

| Waste Composite | Maximum Estimated Organic Content in Kiln Emissions: Assuming no Combustion ppm | g/m³ | From Sample Chromatograms ppb | µg/m³* | Minimum Combustion Efficiency % v/v |
|---|---|---|---|---|---|
| WBA | 550 | 2.40 | 50 | 177.1 | 99.990 |
| WBB | 470 | 3.37 | 50 | 177.1 | 99.989 |
| WBC | 350 | 3.02 | 50 | 177.1 | 99.986 |

*Based on the molecular weight of dichloromethane.

### 5.3.3 Particulate emissions

Summary data for the particulate tests made during each test period are provided in Table 7. For each series of tests, the particulate loadings and emission rates are quite consistent except for the third test in the WBA series. The very high loading obtained probably resulted from some temporary malfunction of the precipitator. It is noticeable that, when the chloride wastes were burned in the kiln, the particulate emission rate increased. For the WBA series, the emission rates were about four times the rates obtained during the baseline tests and for the WBB and WBC series the rates were twice those obtained during the baseline tests.

Increased emission rates were not unexpected since combustion of the chloride wastes produces HCl and $Cl_2$, which react with the alkali components in the raw feed to form volatile alkali chlorides. At the precipitator the particulate loading is, therefore, increased and, since the condensed alkali chlorides are very fine and have a different resistivity, the amount of material passing through the collector increases. Another factor influencing emissions of particulate matter

## TABLE 7. SUMMARY OF PARTICULATE TEST DATA

| Test # | Date | Probe Rinse Gain (mg) | Filter Gain (mg) | Total Gain (mg) | % of Total Gain on Filter | Volume Sampled (std ft$^3$) | Flow rate ACFM | Concentration (grains/ft$^3$) | Emission Rate (lb/hr) |
|---|---|---|---|---|---|---|---|---|---|
| 1 BLA | Oct. 20/75 | 57.6 | 285.7 | 343.3 | 83 | 141.04 | 157,000 | 0.0376 | 20.8 |
| 2 BLA | Oct. 21/75 | 58.8 | 366.0 | 424.8 | 86 | 135.86 | 155,000 | 0.0483 | 25.4 |
| 3 BLA | Oct. 22/75 | 35.8 | 291.8 | 327.6 | 89 | 132.83 | 153,000 | 0.0367 | 19.6 |
| | | | | | | | Average | 0.0409 | 21.9 |
| 1 WBA | Oct. 28/75 | 99.0 | 1242.6 | 1341.6 | 93 | 142.81 | 157,000 | 0.1458 | 83.9 |
| 2 WBA | Oct. 29/75 | 94.8 | 1261.7 | 1356.5 | 93 | 137.34 | 153,000 | 0.1524 | 84.6 |
| 3 WBA | Oct. 30/75 | 237.5 | 2193.8 | 2431.3 | 90 | 109.88 | 165,000 | 0.3415 | 200.0 |
| | | | | | | | Average | 0.2132 | 122.8 |
| 1 WBB | Dec. 10/75 | 143.0 | 424.1 | 567.1 | 75 | 106.64 | 148,000 | 0.0821 | 40.3 |
| 2 WBB | Dec. 11/75 | 86.1 | 468.4 | 554.5 | 84 | 117.06 | 162,000 | 0.0731 | 40.5 |
| 3 WBB | Dec. 12/75 | 145.6 | 621.6 | 767.2 | 81 | 116.24 | 161,000 | 0.1019 | 55.0 |
| | | | | | | | Average | 0.0857 | 45.3 |
| 1 WBC | Jan. 7/76 | 62.2 | 546.3 | 608.5 | 90 | 119.62 | 172,000 | 0.0785 | 45.3 |
| 2 WBC | Jan. 8/76 | 43.1 | 436.5 | 479.6 | 91 | 113.52 | 160,000 | 0.0652 | 34.5 |
| 3 WBC | Jan. 9/76 | 87.8 | 600.0 | 687.8 | 87 | 118.99 | 167,000 | 0.0892 | 52.2 |
| | | | | | | | Average | 0.0776 | 44.0 |
| 1 BLB | Jan. 19/76 | 65.2 | 251.7 | 316.9 | 79 | 126.88 | 183,000 | 0.0385 | 23.9 |
| 2 BLB | Jan. 20/76 | 51.4 | 240.1 | 291.5 | 82 | 116.60 | 163,000 | 0.0386 | 21.0 |
| 3 BLB | Jan. 21/76 | 11.9 | 183.5 | 195.4 | 94 | 116.45 | 168,000 | 0.0259 | 14.6 |
| | | | | | | | Average | 0.0343 | 19.8 |

were the kiln rings formed while burning chlorinated hydrocarbons. Kiln rings, by their effect on gas velocities through the kiln, increase the amount of particulate material carried to the precipitator.

Extensive ring formation was noted during test WBA. The average emission rate for WBA was about 3 lb/ton of clinker produced, compared to the Canadian Federal Government objective of 0.9 lb/ton. The average value for the other phases of the test was about 1.1 lb of particulate emitted/ton of clinker produced and that of the baselines was 0.5. This apparent increase in the particulate emissions while burning chlorinated hydrocarbons is believed to be partially caused by the change in resistivity of the dust entering the precipitator due to its increased alkali content. A modification in the design of the precipitator could compensate for this change.

The higher emission rates did not significantly add to the suspended particulate in the ambient air in the vicinity of the plant. Computed maximum ground level concentrations using standard dispersion equations were less than 2 $\mu g/m^3$ for the baseline emission rates and, during the burning of waste chlorides, did not exceed 10 $\mu g/m^3$. The current Ontario standard is 100 $\mu g/m^3$.

### 5.4 Mass Balance on Wet Kiln

For the wet process kiln, the input streams are slurry feed, No. 6 fuel oil and, when burned, the waste chlorinated hydrocarbons. Clinker (the product) and a portion of the precipitator dust form the output streams. The major portion of the precipitator dust is immediately returned to the process. This stream, though not required for the mass balance, was monitored for information on kiln operation while burning chlorinated hydrocarbons. Balances of chlorine and potassium were calculated for both baseline periods and for each type of chlorinated waste burned. Methods of sampling and quantifying material streams are detailed in Appendix A. Details of analytical results, calculations and tables of daily mass balances are given in Appendix C.

#### 5.4.1 Significance of the mass balance

In common with other material balance experiments on large scale production systems, the material accounting in this experiment showed apparent losses and gains when the data were expressed in percent retention.

These should not be regarded as real system losses or gains. There are random and systematic errors in weighing and quantifying very large quantities of materials and in analytical results. In the case of alkali chlorides, a cycle is developed within the kiln whereby alkali chlorides volatilize in the hotter section of the kiln and condense in the cooler section. Should a kiln upset occur, the cycle may be broken by alkali chloride being retained in the clinker. Such an occurence may be of sufficiently short duration that clinker samples taken may not be indicative. This effect is evident from the data of October 11-14, 1975. A power failure on the eleventh caused a three hour kiln shutdown. The indicated very low retention of both chlorine and potassium occurred presumably while the cycle was being re-established. Since the equilibrium changes when burning of chlorinated materials begins or ends, this feature can also be seen with each phase of chlorinated waste burning. At the start of any chlorinated burn, the mass balance for chlorine indicates very low retention while the cycle is established. At the end of the chlorinated burn, a gain is indicated as chlorine is retained in process solids while the new equilibrium is established. Formation of kiln rings also caused an apparent loss of alkali chloride since a considerable quantity was contained within the ring.

### 5.4.2 Chlorine and potassium retained

The cumulative percentage of chlorine retained (Table 8) was low in all cases throughout the study, ranging from 50.7 percent for the chlorinated aliphatic burn to 92.2 percent for the final baseline. $K_2O$ (Table 9) closely followed the pattern of chlorine retention, although at a different retention level, with 83.5 percent the lowest value found during the chlorinated aliphatic burn and 97.8 percent the highest value found during the final baseline. The reason is clearly that potassium chloride was being lost in ring formation and kiln cycle equilibrium fluctuations.

The cumulative percentage $K_2O$ retained was less affected than that of chlorine by such losses because the quantity of $K_2O$ was from 3 to 20 times greater than the quantity of chlorine. Random and systematic errors could also be expected to play a greater role in the chlorine balance for the same reason.

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TABLE 8. ACCUMULATED MASS BALANCE FOR CHLORINE

| Accumulated Period | Chlorinated Hydrocarbon Burned | Accumulated Input (lb) ($T_I$) | % of $T_I$ From Chlorinated Hydrocarbon | Accumulated Retention (lb) | % Retention |
|---|---|---|---|---|---|
| 7/10/75-22/10/75 | --- | 28,249 | 0 | 20,768 | 73.5 |
| 23/10/75- 4/11/75 | Aliphatic | 134,379 | 83.2 | 68,088 | 50.7 |
| 2/12/75-14/12/75 | Aromatic + Complex | 135,705 | 85.0 | 112,640 | 83.0 |
| 3/ 1/76- 9/ 1/76 | PCB | 58,590 | 82.4 | 41,704 | 71.2 |
| 10/ 1/76-21/ 1/76 | --- | 18,351 | 0 | 16,927 | 92.2 |

TABLE 9. ACCUMULATED MASS BALANCE FOR $K_2O$

| Accumulation Period | Chlorinated Hydrocarbon Burned | Accumulated Input (tons) | Accumulated Retention (tons) | % Retention |
|---|---|---|---|---|
| 7/10/75-22/10/75 | --- | 240.99 | 229.37 | 95.2 |
| 23/10/75- 4/11/75 | Aliphatic | 199.67 | 166.72 | 83.5 |
| 2/12/75-14/12/75 | Aromatic + Complex | 194.59 | 186.68 | 95.9 |
| 3/ 1/76- 9/ 1/76 | PCB | 103.25 | 92.88 | 90.0 |
| 10/ 1/76-21/ 1/76 | --- | 280.40 | 274.36 | 97.8 |

While the chlorine balance does show discrepancies, in all cases while burning chlorinated hydrocarbons more chlorine was retained in process solids than the quantity input with materials other than these wastes. A major portion of the chlorine from the chlorinated hydrocarbon materials is thus accounted for. Considering the uncertainties involved with ring formation and kiln upsets, the mass balance for chlorine confirms the finding of the emission measurements that all chlorinated hydrocarbons are destroyed in the cement kiln.

## 6 CONSIDERATIONS ON BURNING CHLORINATED HYDROCARBON WASTES IN A CEMENT KILN

### 6.1 Effect on Production

Kiln ring formation normally decreases kiln production, apart from any loss of production caused by downtime. However, the kiln rings formed during this study were attributed to poor control of feed rates of the chlorinated waste. Ring formation through chlorine addition rates higher than desirable were previously encountered at St. Lawrence Cement while adding waste hydrochloric acid. Adequate control would certainly eliminate this problem and, since this is a fairly simple proposition, kiln ring formation should not be considered a deterrent to use of this waste in the kiln.

During the study, average production rates (Table 10) were 1038 tons per day while not burning chlorinated hydrocarbons and 1025 tons per day while burning these materials.

There was also an increase of approximately 20 tons per day in the quantity of dust discarded (Table 11) while burning chlorinated materials.

While these values may be partly due to ring formation, it is probable that dust generated would increase due to increased volatilization of alkali chloride, and that this would have a corresponding effect on clinker production. Thus, if another form of chloride were being used for alkali reduction, it is unlikely that any change would be detected by use of chlorinated hydrocarbon wastes.

### 6.2 Alkali Reduction While Burning Chlorinated Hydrocarbon Wastes

As indicated earlier in this report, $Na_2O$ is not considered in this study because it is low and practically constant in the St. Lawrence Cement Co. raw materials and products.

To determine the efficiency of alkali reduction, the following points require consideration. The percent $K_2O$ reported in the slurry feed is on the natural or "as received" basis. To determine the quantity which would be present if none were volatilized in the burning process, the results must be calculated on the "ignited basis", that is, recalculated for the $CO_2$ evolved from the raw materials in the burning process. The

## TABLE 10. AVERAGE REDUCTION IN $K_2O$ CONTENT OF CLINKER

| Accumulation Period | Clinker Prod. (t/day) | Chlorinated Hydrocarbon | Cl Input With Hydrocarbon % Relative to Clinker Prod. | Slurry $K_2O$ (%) | | $K_2O$ Clinker (%) | $K_2O$ Reduction (%) | Calculated* $K_2O$ Reduction (%) |
|---|---|---|---|---|---|---|---|---|
| | | | | Natural Basis | Ignited Basis | | | |
| 7/10/75-22/10/75 | 1056 | - | 0 | 0.92 | 1.42 | 1.21 | 0.21 | 0 |
| 23/10/75- 4/11/75 | 1050 | Aliphatic | 0.41 | 0.92 | 1.42 | 0.87 | 0.55 | 0.58 |
| 2/12/75-14/12/75 | 1020 | Aromatic + Complex | 0.44 | 0.90 | 1.42 | 0.74 | 0.68 | 0.58 |
| 3/ 1/76- 9/ 1/76 | 1006 | PCB | 0.34 | 0.91 | 1.41 | 0.87 | 0.54 | 0.45 |
| 10/ 1/76-21/ 1/76 | 1020 | - | 0 | 0.91 | 1.40 | 1.25 | 0.15 | 0 |

*Based on chlorine input.

TABLE 11. AVERAGE DUST DISCARDED

| Period | Chlorinated Hydrocarbon | Average Dust Discarded (Tons Per Day) |
|---|---|---|
| 7/10/75-22/10/75 | --- | 22.2 |
| 23/10/75- 4/11/75 | Aliphatic | 42.7 |
| 2/12/75-14/12/75 | Aromatic + Complex | 74.0 |
| 3/ 1/76- 9/ 1/76 | PCB | 62.5 |
| 10/ 1/76-21/ 1/76 | --- | 45.1 |

percent $K_2O$ in slurry feed on the ignited basis minus the percent $K_2O$ in the clinker yields the reduction through volatilization in the kiln. Since the $K_2O$ reduction is achieved by formation of potassium chloride (KCl), the reduction expected while burning chlorinated hydrocarbons, based on the assumption that all chlorine is bound into potassium chloride, can be readily calculated. Comparison of actual and calculated values (Table 10) are excellent. If chlorine is added to reduce alkalies, the reduction is stoichiometric. However, the total reduction is relative to alkali levels in the slurry and not to the baseline content in the clinker. This result was confirmed both by this study and by previous experience using hydrochoric acid as the source of chlorine. This may be due to formation of potassium chloride from volatile compounds such as potassium carbonate. On average, without chloride addition, a reduction of 0.18 percent $K_2O$ is apparent. While burning chlorinated hydrocarbons, the average reduction is that calculated on the basis of potassium chloride formation plus 0.05 percent.

The extremely good correlation between quantity of chlorine input by burning of chlorinated hydrocarbons and alkali reduction in the clinker gives better proof than the mass balance that chlorinated hydrocarbons are destroyed in a cement kiln. Otherwise, alkali chloride could not be formed, and volatilization to the extent noted could not occur. The high degree of correlation indicates that all of the chlorinated hydrocarbon was destroyed.

### 6.3 Heat Recovery From Chlorinated Hydrocarbon Wastes

Calculation of heat recovery from these materials, normally difficult due to the low flow rates involved, was made more difficult by the flow control problems encountered. During the aromatic plus complex chlorinated hydrocarbon burn, the oil meter did not function properly and assessment of heat recovery was made only over the first two days of burning. As near as can be established, approximately 65% of the heat of the chlorinated hydrocarbon was recovered (Table 12). This can be expected since volatilization of potassium chloride required energy. While the energy is recovered upon condensation, this occurs too far along the kiln to be completely recuperated. Weber [18] states "volatilization of alkalies consumes high grade heat in the sintering zone and calcining zone above a material temperature of 800°C and this heat is subsequently released only at lower temperatures. Thus, degradation of high-grade heat takes place".

When it is considered that potassium chloride forms a cycle within the kiln and may be volatilized several times before escaping to the precipitator, the heat consumed by this process becomes considerable.

In the suspension preheater kiln, an indication of the number of cycles of volatilization of alkali chlorides is given by the relationship between the Stage IV chloride level and quantity of chloride input. Since in this study, the $K_2O$ at Stage IV was a factor of ten greater than the $K_2O$ input, it follows that ten cycles of volatilization occur on average in the suspension preheater kiln. The situation in the wet process kiln, however, is dissimilar. There is no convenient method for determining the number of alkali cycles involved. That there will not be as many cycles as in the suspension preheater kiln is certain when consideration is given to the differences in the two processes.

It is assumed, for purpose of illustration, that a chlorinated hydrocarbon with 9300 Btu/lb and 42% chlorine is being burned with an alkali cycle of three times. For each pound of chlorinated material, there are 0.42 pounds of chlorine which will produce 0.88 pounds of potassium chloride. The heat of vaporization of potassium chloride is 38,840 cal/mol [19] or 938.6 Btu/lb. The 0.88 pounds of potassium

TABLE 12. RECOVERY OF Btu FROM CHLORINATED HYDROCARBONS

| Material | Average Reduction Input With Oil ($10^6$ x Btu/ton Clinker) | Average Input With Chlorinated Hydrocarbon ($10^6$ x Btu/ton Clinker) | % Useful Heat From Chlorinated Hydrocarbon |
|---|---|---|---|
| Aliphatic | 0.125 | 0.205 | 61 |
| Aromatic + Complex | 0.128 | 0.217 | 59 |
| PCB | 0.157 | 0.228 | 69 |

chloride would require 2478 Btu for three cycles. On this basis we might expect to recover:

$$\frac{9300 - 2478}{9300} \times 100\% = 73\% \text{ of the heat content of the chlorinated}$$

hydrocarbon.

While the above is only an approximation and ignores concurrent heat exchange processes, it indicates that the heat recovery of about 65% obtained in the present study is reasonable.

It should be emphasized that the addition of calcium chloride would require a similar quantity of heat to volatilize alkalies. In the case of calcium chloride, an increase in fuel quantity would be required.

## 6.4 Cement Quality

While the literature available [2, 3, 10] indicates that alkali reduction is beneficial with regard to cement quality, the possibility of unburned organic material being retained in the cement and having a deleterious effect was considered. Cements were ground in the laboratory with clinkers produced while burning only No. 6 fuel oil as well as clinkers produced during the aromatic plus complex and PCB burns. Detailed results are given in Appendix D. The results obtained indicated the only effects to be those due to alkali reduction.

## 6.5 Extrapolation to Other Kiln Types

Since all cement kilns have in common the requirement that uniformly high temperatures be maintained, the authors believe that chlorinated hydrocarbons will be destroyed in all types of cement kilns regardless of fuel used. The only qualification to this statement is that the wastes must be injected into the burning zone. While it is advisable to atomize the chlorinated waste, there appeared to be no difference during the PCB burn with or without a nozzle for atomization.

For fuel economy, cement kilns are operated at low excess oxygen. This, combined with the high temperatures and hydrogen from the fuel, will in all cases ensure that hydrogen chloride (HCl) is preferentially formed rather than free chlorine. In all cement kilns, the lime will readily react with the hydrogen chloride. Based upon results of the present study, no detectable quantities of either compound are expected to be emitted from any type of cement kiln.

Since alkali chloride is volatilized and condensed in the gas stream as extremely fine particles, it would be expected that emission of particulate matter would increase by an amount depending on the efficiency of the precipitator. This would apply to any method of chloride addition. To overcome the plugging problem caused by condensation of these salts in suspension preheaters, design modifications to these units need to be installed and demonstrated.

### 6.6 Comparison of Cement Kiln Burning with Other Uses and Disposal Methods for Waste Chlorinated Hydrocarbons

Information on disposal methods used and actual quantities of chlorinated hydrocarbons requiring disposal is not readily available in Canada. While a conservative estimate of 25-30 million pounds of chlorinated hydrocarbon wastes was obtained, it seems likely that this quantity represents only wastes from plants manufacturing chlorinated hydrocarbon products. The magnitude of the problem of disposal of these wastes in North America can be inferred by some of the methods used. One method makes use of ships designed for burning of these wastes at sea, this method being described in studies monitored by the United States Environmental Protection Agency [20, 21]. Such a method of disposal is expensive, requires constant monitoring of temperatures within the furnace, uses additional fuel for combustion and emits hydrogen chloride (HCl) which is dissolved in the ocean.

Another method of disposal in North America is incineration with production of hydrochloric acid [22].

One report from Europe [23] indicates that methods of disposal are:

1) illegal dumping of small quantities in barrels or other containers on uncontrolled refuse dumps;
2) deposition of larger quantities in barrels on refuse dumps which are supposedly sanctioned for this purpose;
3) combustion in simple facilities without hydrogen chloride scrubbing;
4) combustion of piles of barrels on remote beaches with an offshore wind;
5) dumping barrels on the open sea;
6) dumping liquids into the sea from moving vessels;
7) separation of waste materials and recovery of useful components;
8) combustion with recovery of hydrochloric acid; and,
9) combustion on the open sea at temperatures guaranteeing almost complete pyrolysis.

The same report states: "Only the last three procedures can be considered to be not harmful for the environment. But procedures 7) and 8) are possibly very expensive and in special cases unsustainable for the producer". Also from the same report, it is pointed out that combustion at sea requires extensive observation of a variety of safety procedures.

A study from France [24] indicates that a variety of legal and illegal means are used to dispose of chlorinated hydrocarbon wastes. Of illegal means: "the discharge of what in general are insignificant quantities is disposed of in drums, or by tankers, into waterways, former quarries now used for other purposes, or discharged with unsupervised wastes that reason suggests should be retained".

In comparing combustion in a cement kiln, with other methods of disposal which are considered not harmful to the environment, the following points become apparent:

- Incineration of these wastes is normally done at a flame temperature of 1200°C to 1560°C [25] while cement kiln flame temperatures are 2100°C [18] or higher.

- The retention time in a cement kiln flame envelope is considerably longer than the 0.1 seconds normally found in an incinerator.
- For the production of cement clinker, the temperatures cited are necessary [26], thus removing the necessity for constant monitoring of temperatures as required when burning in an incinerator.
- To prevent operating difficulties, such as kiln rings, in a cement kiln, the amount of chlorine is restricted to approximately 0.4 percent relative to clinker. Besides maintaining constant temperature, this requirement ensures that sufficient hydrogen is available to form hydrogen chloride which is readily absorbed by lime.
- There is always a high quantity of lime in the cement kiln to react with hydrogen chloride and thus prevent emission of this compound to the atmosphere.
- Burning of these wastes in a cement kiln saves fossil fuels, as opposed to the necessity of using fossil fuels to ensure combustion of these wastes in an incinerator.
- Beneficial use is obtained in a cement kiln of persistent and toxic waste materials which normally require disposal.

## 7 CONCLUSIONS

The concept of using chlorinated hydrocarbon wastes in cement processing derives from knowledge of kiln operating temperatures and residence times in comparison with incinerators capable of destroying these compounds. The action of cement kilns as "dry-lime scrubbers" in relation to halogens in the kiln gases was already known.

In all cases, in the present study, analyses of kiln emissions indicated the efficiency of combustion of chlorinated hydrocarbon wastes to have exceeded 99.98 percent. Traces of volatile low molecular weight chlorinated hydrocarbons were found to be present at a maximum emission concentration of 50 ppb above baseline. All other starting materials, including polychlorinated biphenyls, were completely destroyed. There were no detectable emissions of hydrogen chloride, free chlorine or high molecular weight chlorinated hydrocarbons.

An increase in total particulate emissions was observed while burning chlorinated hydrocarbon wastes. This is apparently related to an increase in dust loading to the precipitator as indicated by the necessity of discarding more dust while burning chlorinated hydrocarbons.

Combustion in incinerators designed for destruction of chlorinated hydrocarbon wastes caused the emission of most of the hydrogen chloride except for those installations using expensive hydrochloric acid recovery or scrubbing systems. These incinerators require continous monitoring of temperature profiles and use fossil fuels to initiate or maintain combustion.

The present study indicates that useful recovery of about 65 percent of the heat value and approximately 100 percent of the chlorine is attained by the burning of these wastes in a cement kiln.

A mass balance on chlorine and the effective alkali reduction derived from the chlorine contained in the chlorinated hydrocarbon wastes confirms the air emissions data.

Consideration of the data from this study and examination of the general literature on cement manufacturing has led the authors to conclude that all chlorinated hydrocarbon wastes may be used in cement kilns without adverse effect on air pollution levels.

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# APPENDIX A

## QUANTIFYING, SAMPLING AND ANALYSIS OF PROCESS MATERIALS

While analytical procedures used are identical for both wet and dry process kilns, only the wet process kiln material streams are considered in this Appendix. The dry process suspension preheater kiln system is detailed in Appendix B.

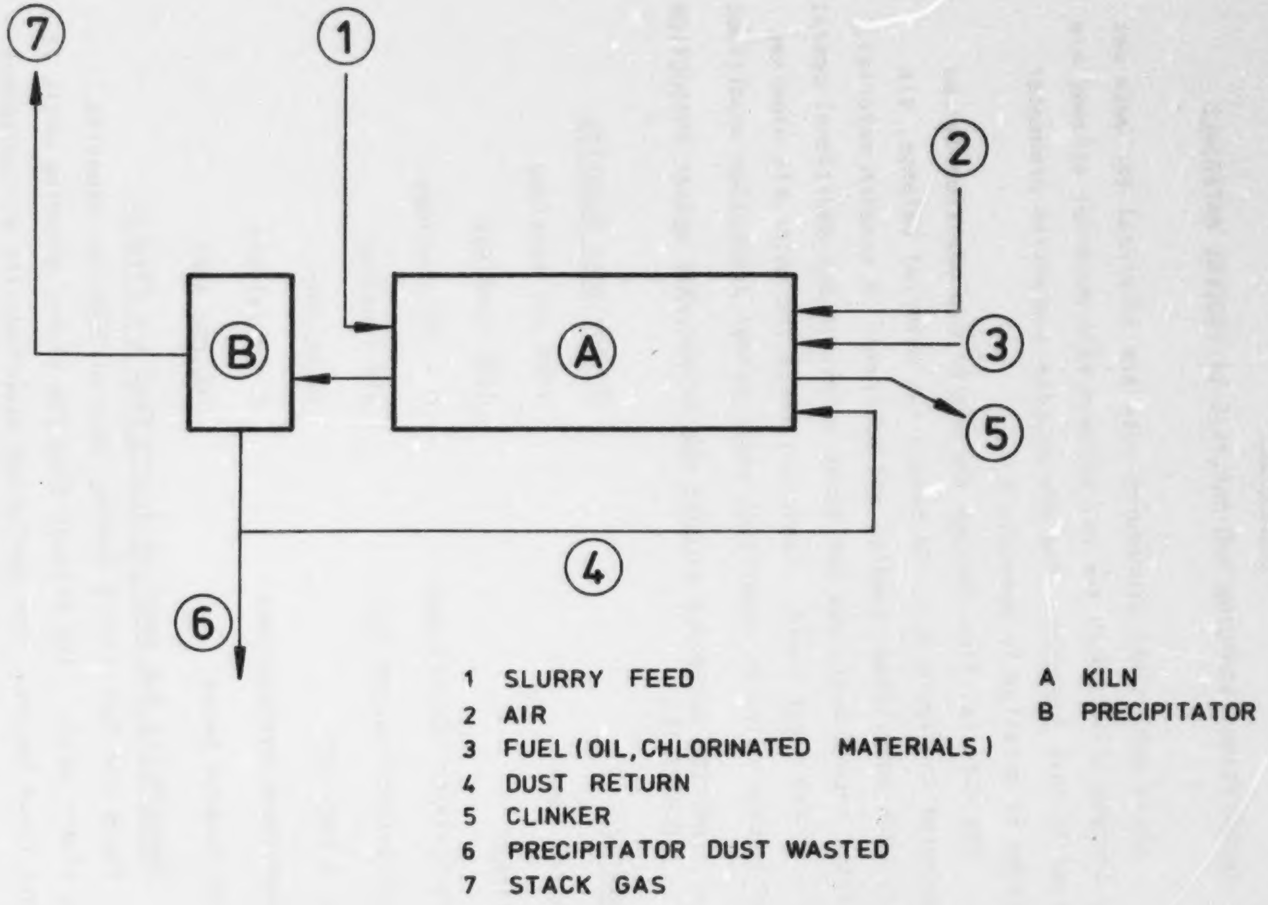
The material flow through the wet kiln production system is illustrated in Figure A.1. To obtain the material balance, six materials were quantified, sampled and analyzed. A seventh material, precipitator return dust, was monitored to obtain any additional operating data this stream might yield. Table A.1 lists the materials examined with approximate relative quantities under normal production conditions.

TABLE A.1. PROCESS MATERIALS STUDIED AND APPROXIMATE NORMAL PRODUCTION QUANTITIES

| Material | Approximate Quantity |
|---|---|
| Slurry Feed | 1540 dry tons/day |
| Clinker | 1000 tons/day |
| Precipitator Discard Dust | 0 - 140 tons/day |
| Precipitator Return Dust | 350 tons/day |
| No. 6 Fuel Oil | 20 gal/min |
| Chlorinated Hydrocarbons | 1 - 2 gal/min |
| Kiln Exhaust Gases | 160,000 ACFM |

### A.1 Quantifying and Sampling Slurry Feed and Clinker

There are four slurry basins, each of 6000 ton capacity, including slurry water. The product from the slurry grinding mills is pumped into these basins. The basins are supplied with air agitators for the purpose of blending the slurry and maintaining a uniform suspension of solids in liquid. Slurry is pumped from one basin at a time to the constant level box of the slurry feed system. The material which over-


7
1
2
B
A
3
5
4
6
1 SLURRY FEED
2 AIR
3 FUEL (OIL, CHLORINATED MATERIALS)
4 DUST RETURN
5 CLINKER
6 PRECIPITATOR DUST WASTED
7 STACK GAS
A KILN
B PRECIPITATOR

SCHEMATIC OF THE MATERIAL BALANCE

FIGURE A.1

flows from the constant level box is returned to the slurry basins. Slurry feed for the kiln is taken from the constant level box by an Allis Chalmers "Ferris Wheel" bucket wheel feeder with variable speed drive. From the bucket wheel feeder, the slurry flows into a small basin with an outlet at the bottom from which the slurry goes directly into the kiln.

The slurry feed samples were taken every two hours from the overflow of the constant level box, and blended into a daily composite. A portion of the daily composite then was dried at 120°C for analysis.

Slurry feed quantities were obtained by multiplying the total number of revolutions of the "Ferris Wheel" per day by a factor. Measurement of the slurry basin levels while feeding the kiln but not allowing slurry to be fed into the basin gives an accurate quantity of slurry fed to the kiln. A second method, performed every two hours, is to close a valve at the outlet to the kiln of the small basin fed by the Ferris Wheel. By determining the time to fill this basin, the quantity fed to the kiln is known.

The clinker is fed to a bucket elevator by gravity through a chute from the cooler. Clinker samples are taken from this chute at intervals of two hours to form a 24-hour composite. The clinker composite sample is mixed, reduced by "cone and quartering" and a portion ground for analysis.

In common with general practice in the industry, there is no provision in the plant for continuous weighing of clinker. The water content of the slurry feed is determined thrice daily, from which the following calculation is made:

$$SFD = SF \left( \frac{100 - H_2O}{100} \right)$$

where $SFD$ = quantity of slurry feed on a dry basis

$SF$ = quantity of slurry feed including water

$H_2O$ = % water in the slurry feed.

To obtain the quantity of clinker produced, the $CO_2$ which is lost in the burning process (determined by loss on ignition of the dry slurry feed) is deducted and a further correction is made for the quantity of dust discarded from the system. A total material balance may then be written as follows:

$$\text{Clinker} = \text{SFD}\left(\frac{100 - \text{LOI}_{\text{SFD}}}{100}\right) - \text{DD}\left(\frac{100 - \text{LOI}_{\text{DD}}}{100}\right)$$

where SFD = quantity of slurry feed on dry basis

$\text{LOI}_{\text{SFD}}$ = % loss on ignition on slurry feed on dry basis

DD = quantity of dust discarded

$\text{LOI}_{\text{DD}}$ = % loss on ignition on dust discarded.

## A.2 Weighing and Sampling Precipitator Dust

Dust from the precipitator is separated into two portions by a system of screw conveyers under the precipitator. The major portion is returned via a conveyor belt into a small holding silo from which the dust is returned into the burning zone of the kiln (return dust). Samples of the dust are taken at two-hour intervals from the conveyor belt to form a 24-hour composite. The composite is blended and a portion taken for analysis. A minor portion of the dust (discard dust) is fed into a second holding silo from which trucks are loaded directly. A sample of this dust is taken from each truck load, and all samples for each day are blended into a 24-hour composite. Each load of dust is weighed on the truck weigh scales before being disposed of.

## A.3 Measurement and Sampling No. 6 Fuel Oil

While it was considered unlikely that No. 6 fuel used in the plant would contribute a substantial quantity of chlorine, samples of oil were taken daily. Fuel quantities are continuously monitored and recorded in the production data but are not given in this report. Chlorine content of the oil was determined, and the contribution to the chlorine mass balance due to oil was included.

## A.4 Measurement and Sampling Waste Chlorinated Hydrocarbons

Sampling of chlorinated hydrocarbons was carried out by withdrawing material from the feed system twice daily and blending by vigorous mixing. Samples were split into equal portions after blending.

Initially, it was intended to meter chlorinated hydrocarbon flow continuously. For this purpose, a magnetic flow meter was installed in the line to monitor quantities of these materials. For this type of meter to function properly, it is required that the conductivity of the material be greater than $2 \times 10^{-6}$ mhos. While this was the case for the chlorinated aliphatic wastes, the conductivities of the other materials were less than $0.3 \times 10^{-6}$ mhos. As a result, chlorinated waste material quantities were determined by taking measurements of the volume of material in the storage tank. Tables A.2 through A.4 give detailed information on calculated chlorinated waste material quantities.

### A.5 Emission Sampling

Separate sampling trains were used to collect representative samples of kiln emissions for analysis to determine the emission rates of particulate material and to determine if organic chloride compounds were present in the gas stream passing to the stack. Particulate and gaseous samples were collected from a duct downstream of the precipitator controlling dust emissions from kiln #1. The location is described below, followed by descriptions of sampling equipment and methodology.

### A.5.1 Sampling location

Emissions from both #1 and #2 wet process kilns pass through electrostatic precipitators (Joy Manufacturing Co.) and then through sections of rectangular breeching before mixing in a common section of duct entering the stack. The stack, which is of height 554.0 feet and has an exit diameter of 13.0 feet, vents the exhaust gases to the atmosphere at a temperature of about 400°F and a velocity of almost 40 feet per second.

The rectangular breeching from the precipitator makes a 90° bend and then angles at about 30° upwards from the horizontal for a distance of approximately 45 feet to the common header which leads into the stack. This 45 foot section of duct was considered the most suitable for installation of sampling ports at a location which would meet both Federal and Provincial source testing codes. It was subsequently decided, therefore, to install five 4" diameter ports in the vertical side of the duct at a position 12 feet upstream of the bend into the

## TABLE A.2. QUANTITIES OF ALIPHATIC MIXTURE BURNED DAILY

| Date | Time From | To | Minutes | Igpm | Gallons | Gallons/Day |
|---|---|---|---|---|---|---|
| 23/10/75 | 09:00 | 12:00 | 180 | 0.5 | 90 | 1170 |
| | 12:00 | 06:00 | 1080 | 1 | 1080 | |
| 24/10/75 | 06:00 | 06:00 | 1440 | 1 | 1440 | 1440 |
| 25/10/75 | 06:00 | 06:00 | 1440 | 1 | 1440 | 1440 |
| 26/10/75 | 06:00 | 06:00 | 1440 | 1 | 1440 | 1440 |
| 27/10/75 | 06:00 | 06:00 | 1440 | 1 | 1440 | 1440 |
| 28/10/75 | 06:00 | 06:00 | 1440 | 1 | 1440 | 1440 |
| 29/10/75 | 06:00 | 06:00 | 1440 | 1 | 1440 | 1440 |
| 30/10/75 | 06:00 | 09:30 | 210 | 1 | 210 | 2670 |
| | 09:30 | 06:00 | 1230 | 2 | 2460 | |
| 31/10/75 | 06:00 | 06:00 | 1440 | 2 | 2880 | 2880 |
| 1/11/75 | 06:00 | 06:00 | 1440 | 2 | 2880 | 2880 |
| 2/11/75 | 06:00 | 06:00 | 1440 | 2 | 2880 | 2880 |
| 3/11/75 | 06:00 | 06:00 | 1440 | 2 | 2880 | 2880 |
| 4/11/75 | 06:00 | 10:00 | 240 | 2 | 480 | 930 |
| | 10:00 | 17:30 | 450 | 1 | 450 | |
| | OFF | at 17:30 | | | | |

## TABLE A.3. QUANTITIES OF AROMATIC PLUS COMPLEX MIXTURE BURNED DAILY

| Date | Time | Tank Measurement | Difference gallons | Difference minutes | Gal/min |
|---|---|---|---|---|---|
| Dec. 6 | 15:00 | 12' 0" | | | |
| | 2 loads in 60930 lb + 40690 lb @ 1.299 SG = 7823 gal | | | | |
| Dec. 7 | 12:15 | 14' 6" | (7823-5886 = 1937 gal) | | |
| | | | 1937 | 1275 | 1.519 |
| Dec. 8 | 15:00 | 14' 0" | 1177 | 1605 | 0.733 |
| Dec. 9 | 15:30 | 13' 6" | 1177 | 1470 | 0.801 |
| Dec. 10 | 12:00 | 12' 6" | 2354 | 1230 | 1.914 |
| Dec. 11 | 15:00 | 11' 8" | 1962 | 1620 | 1.211 |
| Dec. 12 | 09:00 | 11' 4" | 785 | 1080 | 0.727 |
| Dec. 12 | 15:30 | 11' 0" | 785 | 390 | 2.013 |
| Dec. 13 | 13:30 | 10' 3" | 1373 | 1320 | 1.040 |
| Dec. 14 | 13:20 | 9' 6" | 1766 | 1430 | 1.235 |
| Dec. 15 | 14:00 | 8' 8" | 1962 | 1480 | 1.326 |

### Gallons per Day

| Date | From | To | Minutes | Igpm | Gallons | Total Gallons |
|---|---|---|---|---|---|---|
| Dec. 2 | 06:00 | 13:10 | 430 | (1) | 430 | 430 |
| Dec. 5 | 10:00 | 12:00 | 120 | 1.519 | 182 | 1640 |
| | 14:00 | 06:00 | 960 | 1.519 | 1458 | |
| Dec. 6 | 06:00 | 06:00 | 1440 | 1.519 | 2187 | 2187 |
| Dec. 7 | 06:00 | 12:15 | 375 | 1.519 | 570 | 1351 |
| | 12:15 | 06:00 | 1065 | 0.733 | 781 | |
| Dec. 8 | 06:00 | 15:00 | 540 | 0.733 | 396 | 1117 |
| | 15:00 | 06:00 | 900 | 0.801 | 721 | |
| Dec. 9 | 06:00 | 15:30 | 570 | 0.801 | 456 | 2121 |
| | 15:30 | 06:00 | 870 | 1.914 | 1665 | |
| Dec. 10 | 06:00 | 12:00 | 360 | 1.914 | 689 | 1997 |
| | 12:00 | 06:00 | 1080 | 1.211 | 1308 | |

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TABLE A.3. (Cont'd)

| Date | From | To | Minutes | Igpm | Gallons | Total Gallons |
|---|---|---|---|---|---|---|
| Dec. 11 | 06:00 | 15:00 | 540 | 1.211 | 654 | 1308 |
| | 15:00 | 06:00 | 900 | 0.727 | 654 | |
| Dec. 12 | 06:00 | 09:00 | 180 | 0.727 | 131 | 1821 |
| | 09:00 | 15:30 | 390 | 2.013 | 785 | |
| | 15:30 | 06:00 | 870 | 1.040 | 905 | |
| Dec. 13 | 06:00 | 13:30 | 450 | 1.040 | 468 | 1691 |
| | 13:30 | 06:00 | 990 | 1.235 | 1223 | |
| Dec. 14 | 06:00 | 13:20 | 440 | 1.235 | 543 | 1869 |
| | 13:20 | 06:00 | 1000 | 1.326 | 1326 | |
| Dec. 15 | 06:00 | 06:00 | 1440 | 1.326 | 1909 | 1909 |

## TABLE A.4. QUANTITIES OF PCB MIXTURE BURNED DAILY

| Date | Time | Tank Measurement | Difference gallons | Difference minutes | Gal/min |
|---|---|---|---|---|---|
| 3/1/76 | 14:30 | 11' 4" | | | |
| 4/1/76 | 12:00 | 12' 6" | 1962 | 1290 | 1.521 |
| 5/1/76 | 09:15 | 9' 8" | 1962 | 1275 | 1.539 |
| 5/1/76 | 14:30 | 9' 6" | 392 | 315 | 1.244 |
| 6/1/76 | 09:10 | 8' 7" | 1766 | 1120 | 1.577 |
| 7/1/76 | 09:06 | 7'11" | 1962 | 1436 | 1.366 |
| 7/1/76 | 16:00 | 7'10" | 196 | 414 | 0.473 |
| 8/1/76 | 08:45 | 7' 9" | 196 | 1003 | 0.195 |
| 8/1/76 | 15:45 | 7' 8" | 196 | 420 | 0.467 |
| 9/1/76 | 08:45 | 7' 2" | 1177 | 1020 | 1.154 |
| 9/1/76 | 05:45 | 6' 8" | 1177 | 540 | 2.180 |

Gallons per Day

| Date | From | To | Minutes | Igpm | Gallons | Total Gallons |
|---|---|---|---|---|---|---|
| 3/1/76 | 07:45 | 14:30 | 405 | 1.521 | 616 | 2030 |
| | 14:30 | 06:00 | 430 | 1.521 | 1414 | |
| 4/1/76 | 06:00 | 12:00 | 360 | 1.521 | 548 | 2210 |
| | 12:00 | 06:00 | 1080 | 1.539 | 1662 | |
| 5/1/76 | 06:00 | 09:15 | 195 | 1.539 | 300 | 2159 |
| | 09:15 | 14:30 | 315 | 1.244 | 392 | |
| 6/1/76 | 06:00 | 09:10 | 190 | 1.577 | 300 | 2008 |
| | 09:10 | 06:00 | 1250 | 1.366 | 1708 | |
| 7/1/76 | 06:00 | 09:06 | 186 | 1.366 | 254 | 614 |
| | 09:06 | 16:00 | 414 | 0.473 | 196 | |
| | 16:00 | 06:00 | 840 | 0.195 | 164 | |
| 8/1/76 | 06:00 | 08:45 | 165 | 0.195 | 32 | 1215 |
| | 08:45 | 15:45 | 420 | 0.467 | 196 | |
| | 15:45 | 06:00 | 855 | 1.154 | 987 | |
| 9/1/76 | 06:00 | 08:45 | 165 | 1.154 | 190 | 1433 |
| | 08:45 | 18:15 | 570 | 2.180 | 1243 | |

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header, and positioned on a line perpendicular to the gas flow. The port locations are shown schematically in Figure A.2.

As agreed upon by the Ontario Ministry of Environment and Environment Canada, sampling was carried out at eight points on each of the five duct traverses for a minimum of five minutes per point. The sampling points were located at the centres of equal rectangular areas in the duct as shown in Figure A.3. The numbers given in each rectangle are typical gas velocities measured during the study and indicate the distribution of gas flow at that location.

### A.5.2 Sampling equipment

Prior to setting up equipment for particulate and gaseous sampling, grab samples of the kiln emissions were taken using the equipment depicted in Figure A.4. A gas sample was pulled through an in-stack 47 mm glass fibre filter in a stainless steel holder to remove particulate material and then through a heated teflon line into a Tedlar bag. For each bag sample a clean bag was placed in the lung and the lid tightened to effect an air-tight seal. Valves A and C were closed and B opened so that, with the pump on, the sampling line was purged. Valve B was then closed and valve C opened to evacuate the sampling lung, making sure that the vacuum did not exceed 5" Hg. At a vacuum of 4" Hg, valve A was opened and the sample bag filled with emissions from the duct. Valve A was then closed and valve B opened. The pump was shut off and the line to the pump disconnected. Valve C was opened to bring the lung to atmospheric pressure and the bag was removed from the drum and quickly capped. Each bag sample was transported to the laboratory at ORF for analysis on the same day that the sample was collected.

A.5.2.1 Particulate train. Samples of particulate emissions were collected using a Joy Manufacturing Company EPA (Model CU-2) train, shown schematically in Figure A.5. This equipment conforms to that recommended by both the Ontario Source Testing Code [A.1] and the Environment Canada Code [A.2]. Prior to each test a velocity traverse was conducted across the duct through each part to determine an average gas velocity. Gas temperatures were also recorded at each sample point.

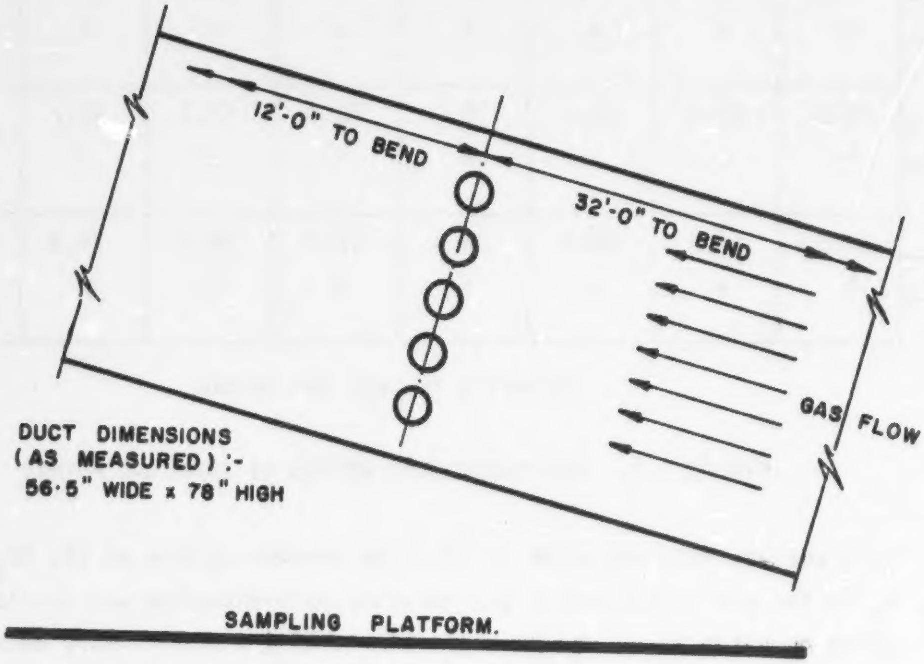
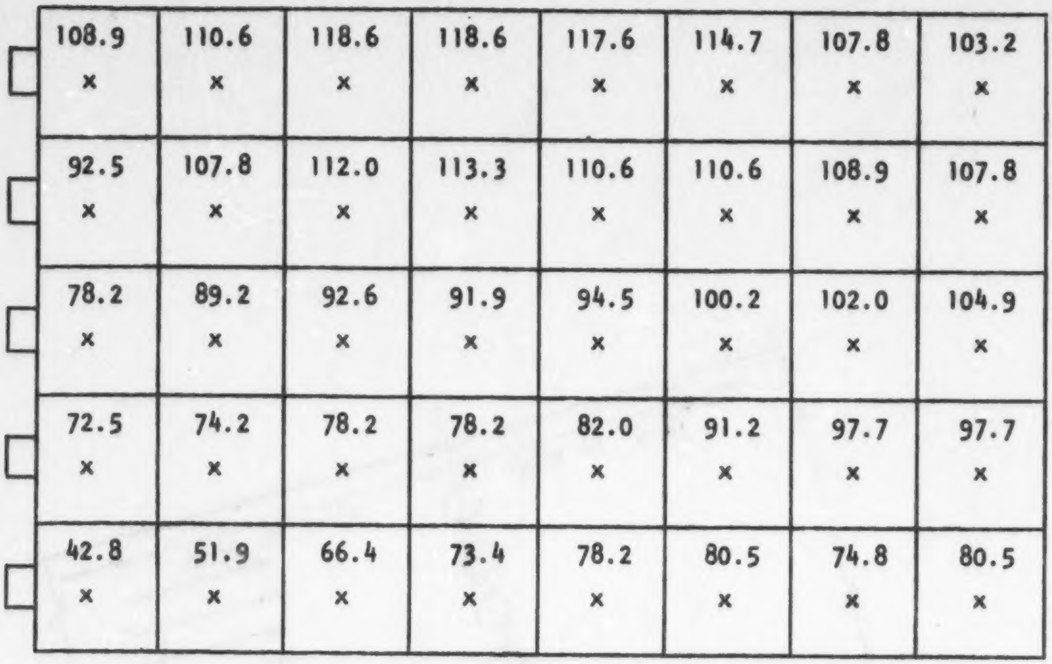

12'-0" TO BEND
32'-0" TO BEND
GAS FLOW
DUCT DIMENSIONS
(AS MEASURED) :-
56·5" WIDE x 78" HIGH
SAMPLING PLATFORM.

FIGURE A.2. SCHEMATIC OF PORT LOCATIONS



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 108.9<br>× | 110.6<br>× | 118.6<br>× | 118.6<br>× | 117.6<br>× | 114.7<br>× | 107.8<br>× | 103.2<br>× |
| 92.5<br>× | 107.8<br>× | 112.0<br>× | 113.3<br>× | 110.6<br>× | 110.6<br>× | 108.9<br>× | 107.8<br>× |
| 78.2<br>× | 89.2<br>× | 92.6<br>× | 91.9<br>× | 94.5<br>× | 100.2<br>× | 102.0<br>× | 104.9<br>× |
| 72.5<br>× | 74.2<br>× | 78.2<br>× | 78.2<br>× | 82.0<br>× | 91.2<br>× | 97.7<br>× | 97.7<br>× |
| 42.8<br>× | 51.9<br>× | 66.4<br>× | 73.4<br>× | 78.2<br>× | 80.5<br>× | 74.8<br>× | 80.5<br>× |

Velocity in feet per second

FIGURE A.3. GAS FLOW DISTRIBUTION AT SAMPLING POINTS

An Orsat analysis was made to find the concentrations of CO, $CO_2$, $O_2$ and $N_2$ in the gas stream and a gas moisture determination was carried out using an established procedure [A.1]. With the preliminary data obtained, the isokinetic sampling rate was calculated using known standard equations [A.1].

For each particulate test, sampling was made for five minutes at each of the eight points across the duct through the five ports. Specified data [A.1] were recorded every 2.5 minutes on a test data sheet. The high flow rates encountered at the far wall of the duct and across the top of the duct necessitated use of probe nozzles of diameter less than 0.25 inches. Nozzles of diameter 0.219 inches and 0.188 inches were used during certain tests.

At the conclusion of a test the glass fibre filter was removed from its holder and placed in a labelled petri dish. The volume of water in the impingers was measured and the contents transferred

7

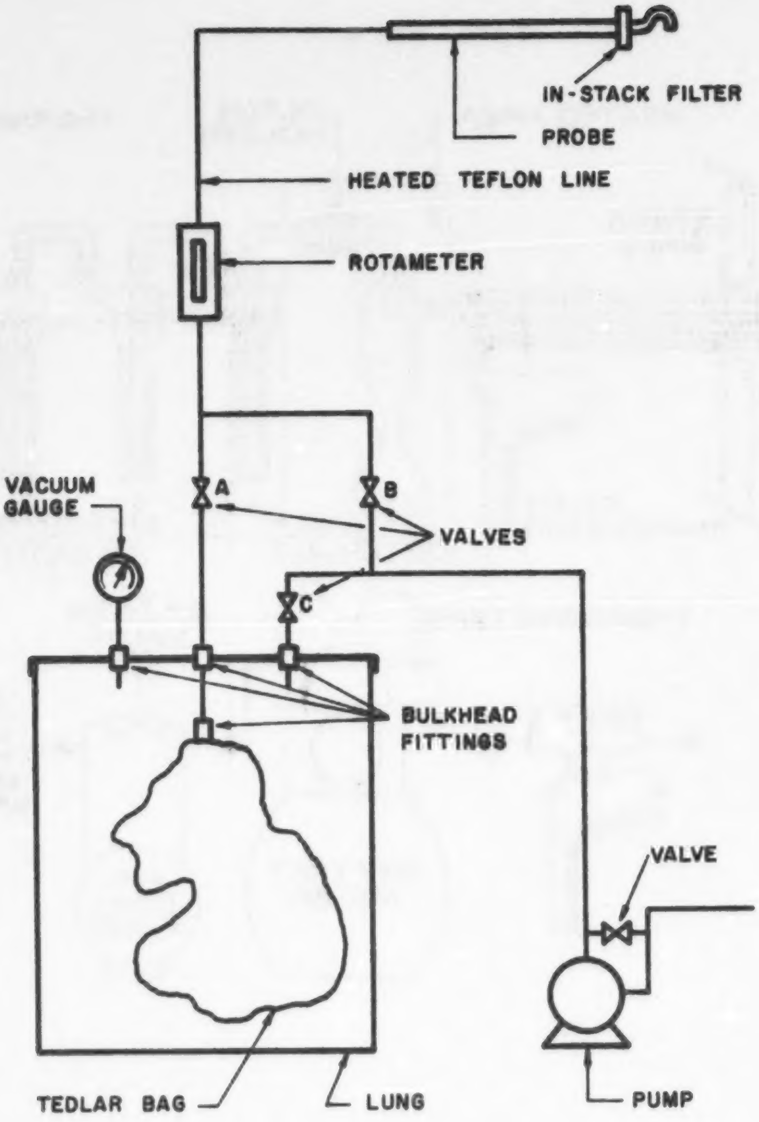

IN-STACK FILTER
PROBE
HEATED TEFLON LINE
ROTAMETER
VACUUM GAUGE
A
B
VALVES
C
BULKHEAD FITTINGS
VALVE
TEDLAR BAG
LUNG
PUMP

FIGURE A.4. GRAB BAG SAMPLING EQUIPMENT

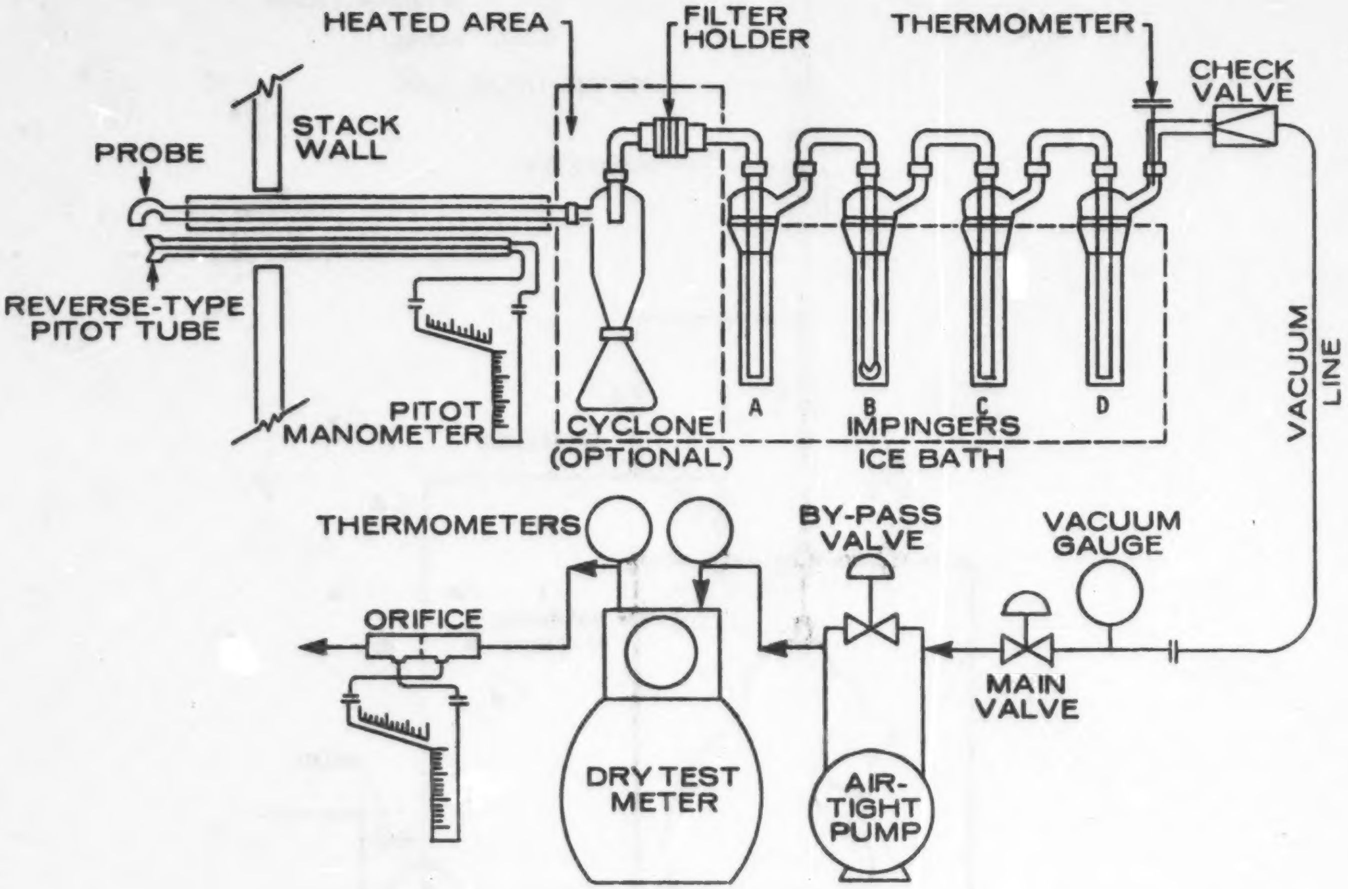

HEATED AREA
FILTER HOLDER
THERMOMETER
CHECK VALVE
STACK WALL
PROBE
REVERSE-TYPE PITOT TUBE
PITOT MANOMETER
CYCLONE (OPTIONAL)
A
B
C
D
IMPINGERS
ICE BATH
VACUUM LINE
THERMOMETERS
BY-PASS VALVE
VACUUM GAUGE
ORIFICE
MAIN VALVE
DRY TEST METER
AIR-TIGHT PUMP

FIGURE A.5. PARTICULATE SAMPLING TRAIN

to polyethylene bottles, which were then labelled. The probe and nozzle were rinsed with distilled water as the inside of the probe was carefully brushed. The rinsings were collected in a polyethylene bottle. The glassware between the end of the probe and top of the filter holder was washed with distilled water and these washings added to the probe rinse. The bottom of the filter holder and glassware between filter and impingers was also washed and the contents added to the impinger catch.

After filtering the probe rinse, drying and weighing the insoluble particulate material, weighing the reconditioned filter, and determining the soluble portion of particulates in the probe rinse by aliquot evaporation, the total weight of collected particulate material was obtained. The moisture removed from the sampled gas was found by adding the gain in weight of the silica gel to the volume of additional water collected in the impingers. The volume of gas sampled was corrected to standard conditions and the particulate loading and emission rate calculated by use of appropriate equations [A.1].

A.5.2.2 Gaseous train. It was originally intended to sample for gaseous organic chloride compounds using the EPA-type particulate train, with specific absorbents replacing water in the impingers. Due to the high flow rates (0.5 - 1.0 cfm) required for isokinetic sampling, however, it was considered that the collection efficiency of any absorbent for volatile organic compounds would be very low. An experimental program was, therefore, devised and carried out at ORF to evaluate collection methods and develop a suitable sampling train for gaseous organic chlorides. Details of this study, performed under contract to the Ontario Ministry of the Environment, are given in Appendix H. Data obtained which are relevant to this section are described below.

A particulate train was set up in the laboratory and heated air was pulled through the complete system at a flow rate of 0.5 cfm. Water was placed in the first impinger and solvents such as xylene, toluene and decane, containing a few ppm of $CHCl_3$, $CH_2Cl_2$ or $CHCl_2CH_2Cl$, were placed in the second impinger. The third impinger was left empty and the fourth contained silica gel. After a period of three to four hours, the time anticipated for a particulate test, the impingers were examined with respect to solvent volume and organic chloride concentration. In all cases, it was found that the loss of chloride compounds was considerable. For the polar solvents, such as toluene or xylene, the chloride concentration was retained but the total loss of solvent plus chlorides was in the range of 50%-70%. For the non-polar solvents, such as decane, the volume loss of solvent was negligible but the chloride loss was in the range of 60%-90%. Even if efficient collection of trace organic chlorides from the gas stream by specific solvents were possible, these compounds would not be retained in solution at gas flow rates of 0.5 cfm or higher.

Recent studies have shown that collection and retention of trace organic compounds is possible using specific adsorbent materials [A.3]. Inert materials, such as the Chromosorbs, are considered to have certain advantages over activated carbons in that water vapour present in the gas does not hinder organic compound adsorption, and adsorbed compounds are readily removed by thermal desorption. Experiments using the particulate train with Chromosorb 102 or activated carbon in the third impinger were carried out, passing heated air containing a few ppm of $CHCl_3$ through the system at a flow rate of 0.5 cfm. Neither adsorbent removed more than 70% of the $CHCl_3$ initially and, after about thirty minutes, almost all of the $CHCl_3$ was passing through the system. It was concluded, therefore, that efficient collection and retention of volatile organic compounds was not possible with gas flow rates of 0.5 cfm or higher and the particulate train could not be used for this purpose.

After further studies in the laboratory with both Chromosorb 102 and activated carbon, the sampling train for gaseous organic compounds depicted in Figure A.6 was constructed. Tests made with an air stream containing 15 ppm of $CHCl_3$ showed that either adsorbent would remove better than 95% of the $CHCl_3$ over a sampling period of four hours. Chromosorb 102 was selected on the basis of the advantages previously mentioned.

A 47 mm fibreglass filter was placed directly behind the probe nozzle to remove particulate material at the duct gas temperature. The sample gas was passed through midget impingers containing water and

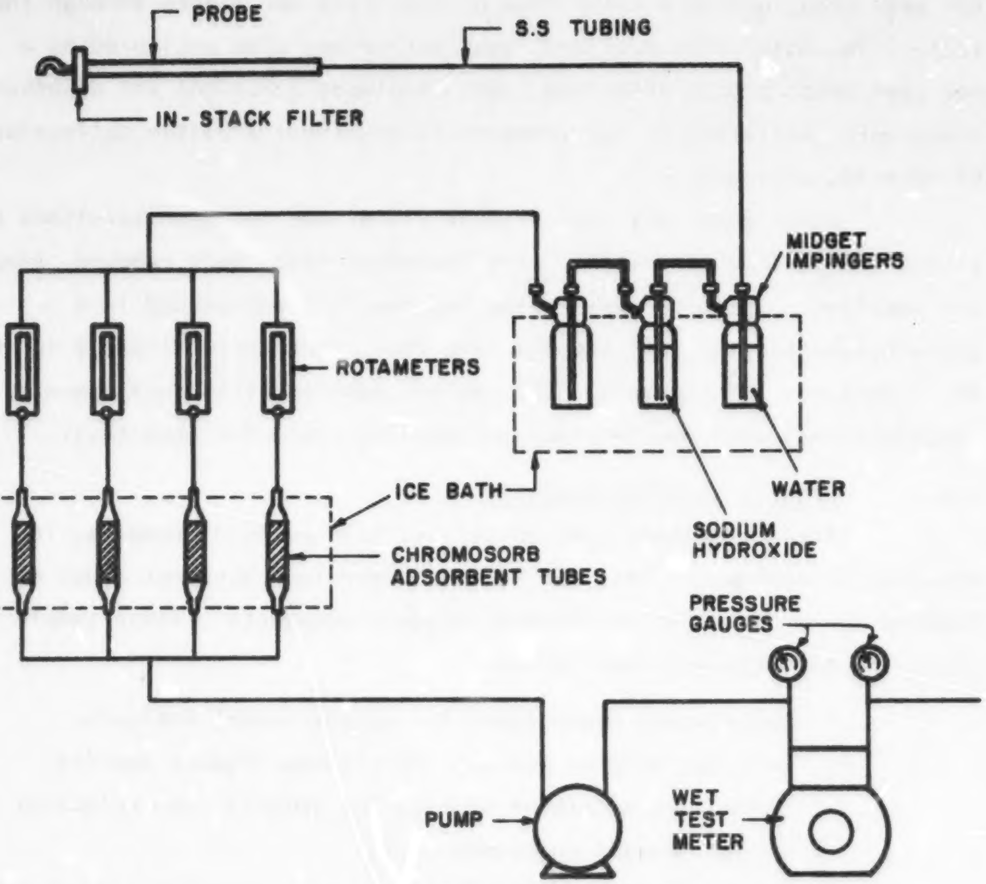

PROBE
S.S TUBING
IN- STACK FILTER
MIDGET IMPINGERS
ROTAMETERS
ICE BATH
WATER
SODIUM HYDROXIDE
CHROMOSORB ADSORBENT TUBES
PRESSURE GAUGES
PUMP
WET TEST METER

FIGURE A.6. GASEOUS SAMPLING TRAIN

caustic soda (5% solution), respectively, to remove any HCl and $Cl_2$ present in the kiln emissions. After the impinger, the gas was filtered through four Chromosorb adsorbent traps placed in parallel at a flow rate controlled by rotameters. A flow rate of 250 ml per minute was selected for each trap, giving a total flow of one litre per minute through the train. The total flow over each test period was also monitored by a wet test meter placed after the pump. Impinger solutions and adsorbent traps were maintained at ice temperature to effect a better collection of chloride compounds.

After each test the in-stack filter and impinger solutions were stored in labelled containers. The adsorbent traps were removed, capped and labelled. The probe was rinsed and the rinsings placed in a polyethylene bottle. All samples were then transferred directly to the ORF laboratory for analysis. The gaseous sampling train was operated simultaneously with the particulate sampling train for each test.

## A.6 Organic Chloride Analyses

The methodology used to collect kiln emission samples, in baseline or waste burn test periods, provided four distinct types of samples for analysis of chlorinated organic compounds. These sample types and the analyses required were:

- chlorinated waste feeds for compositional analysis;
- grab bag samples for any chlorinated organic species;
- Chromosorb adsorbent samples for volatile low molecular weight organic compounds; and,
- solvent extracts of filters and solutions for noncombusted waste components.

### A.6.1 Sample preparation

Waste feed. Samples of the prospective WBA feed material were supplied in advance of the test burn for analyses. When the test period arrived, however, insufficient quantities of some components were available to make up the specific blend of waste feed. The composition of material actually delivered to SLC was, therefore, different from the sample supplied to ORF in advance. In order to obtain a true compositional analysis of the material being supplied to the kiln, and to determine feed consistency, aliquots of the waste feed were collected on specific sampling days during the burn.

Grab bag. Emission samples collected in Tedlar bags were analyzed directly for gaseous chlorinated hydrocarbons by injecting syringe samples taken from the bag into a gas chromatograph. After direct analysis, the contents of each bag were drawn through a glass tube containing Chromosorb 102 adsorbent by means of a small pump. Any trapped organic compounds were then thermally desorbed from the adsorbent tube into an evacuated gas jar. The gas jar contents were then subjected to GC analysis.

Adsorbent tubes. Chromosorb 102, being readily available in amounts required for this study, was selected as a suitable adsorbent for low molecular weight organohalides. Experiments were performed in the laboratory to confirm the suitability and efficiency of this adsorbent for the collection of volatile organohalides from an air stream. Thermal desorption of adsorbed components into an evacuated gas jar was selected as a method for preparing samples for GC analysis. Initial tubes were prepared with fresh Chromosorb 102 from the bottle without conditioning. It was determined after the first baseline test period that conditioning of the adsorbent would be necessary to reduce the amount of bleed produced on heating which tended to produce excessive background noise during GC analysis.

Adsorbent tubes were made up by packing Chromosorb 102 in glass containers 11.5 cm in length and 11.0 mm inside diameter, using silanized glass wool plugs at either end for support. Tubes for the WBA and WBB burns were preconditioned by heating to 200°C and passing a stream of nitrogen at 40 ml/min through them for four hours. Chromosorb 102 used in tubes for the WBC and BLB tests was extracted with acetone in a Soxhlet for 18 hours and then treated at 240°C with nitrogen for 12 hours prior to use.

Adsorbed components on the Chromosorb 102 after each test were removed by thermal desorption into an evacuated gas jar of 500 ml capacity. The adsorbent tube and gas jar were connected by Teflon tubing and the tube heated to a fixed temperature of 170°C using a heating tape controlled by a variable transformer. When the fixed temperature was reached the stopcock of the gas jar between the jar and the tube was opened, and heating of the tube continued for a further 15 minutes. The stopcock was then closed, the jar removed from the connecting tubing and taken outside the laboratory to fill up with clean air. Previous studies of thermal desorption using this removal technique in the laboratory have shown that recoveries in excess of 90% may be expected for adsorbents with adsorbed organohalides.

Solution and filter extracts. Pentane or hexane was used as an extractant for organic compounds from all filters and probe rinse insoluble fractions, using a Soxhlet apparatus. The same solvents were used to extract probe rinse solutions, and aqueous sodium hydroxide and impinger solutions, using a liquid/liquid partitioning procedure. The extracts were then dried over anhydrous $Na_2SO_4$, filtered, and concentrated by evaporation using a combination of rotary and Kontes tube heaters. The concentrate was made up to a known small volume with solvent for GC analysis.

Pentane was used as extractant for BLA, WBA and WBB test samples, since its high volatility would minimize sample loss of low molecular weight compounds during evaporation. Hexane was used as extractant for WBC and BLB test samples.

### A.6.2 Sample analysis

All samples were analyzed by gas chromatography with flame ionization (FI) or electron capture (EC) detectors. Gas chromatography - mass spectrometric (GC-MS) analysis was performed on waste feed samples to confirm the identity of major components. The various conditions and columns used are summarized in Tables A.5 to A.7. The mass spectrometer used was an AEI MS-30 instrument equipped with an electron bombardment ion source. Between the GC and the MS the interface is of all glass design with a silicone molecular membrane. GC columns similar to those described in Tables A.5 to A.7 were used at approximately the same instrument conditions.

## TABLE A.5. GC ANALYSIS - SYSTEM A

| | |
|---|---|
| Column | Chromosorb 102 (80/100 mesh) 6' x 1/8'' SS |
| Column Temperature | 180°C |
| Injector Temperature | 215°C |
| Detector Temperature | 215°C |
| Detector | FID and EC |
| Flow Rates | $N_2$ at 40 ml/min<br>Air and $H_2$ adjusted for maximum sensitivity |
| Range and Attenuation | As required |
| Chart Speed | As required |

## TABLE A.6. GC ANALYSIS - SYSTEM B

| | |
|---|---|
| Column | 15% SE 30 on Chromosorb W (AW; HDMS; 60/80 mesh) 12' x 1/4'' SS |
| Column Temperature | 60°C isothermal for 20 minutes then programmed at 10°C/min to maximum temperature |
| Injector Temperature | 190°C |
| Detector Temperature | 230°C |
| Detector | FID |
| Flow Rates | $N_2$ at 40 ml/min<br>Air and $H_2$ adjusted for maximum sensitivity |
| Range and Attenuation | As required |
| Chart Speed | As required |

TABLE A.7. GC ANALYSIS - SYSTEM C

| | |
|---|---|
| Column | 4% SE 30/6% QF 1 on Chromosorb W (HP; 60/80 mesh) 6' x 1/8" SS |
| Column Temperature | 200°C |
| Injector Temperature | 250°C |
| Detector Temperature | 230°C |
| Detector | Linearized EC |
| Flow Rates | $N_2$ at 25 ml/min |
| Range and Attenuation | As required |
| Chart speed | As required |

These conditions are used for routine PCB analyses. The same parameters were used for WBB waste feed except that an isothermal temperature of 155°C was maintained.

### A.6.3 Blanks and standards

For trace analytical studies it is necessary to avoid contamination of samples at all stages of sample collection and preparation. Though extreme care was taken during the study it was not possible to pre-extract all hardware and chemical reagents used. Due to the high sensitivity of the EC detector to many compounds, some of the blank extracts, therefore, gave complex GC-EC profiles, which had to be subtracted as background from the sample chromatograms. The following blanks were obtained and analyzed for this purpose.

i) Particulate train:
   (a) Particulate filter + probe rinse filter + Soxhlet thimble.
   (b) Water

ii) Gaseous train:
   (a) In-stack filter + probe rinse filter + Soxhlet thimble
   (b) Water
   (c) Aqueous NaOH

iii) Solvents:
   (a) Pentane (100 ml concentrated to 1 ml)
   (b) Hexane (100 ml concentrated to 1 ml)

iv) Polyethylene containers: (a) Solvent extracts (100 ml concentrated to 1 ml)

Standard gas samples of various components of interest, such as $CCl_4$, $CHCl_3$, $CH_2Cl_2$ and 1,2-dichloroethane, were made by injecting 50 μl aliquots of these compounds into an evacuated 500 ml gas jar through a silicone septum. Clean air was then allowed to enter the jar to attain atmospheric pressure. The sealed gas jar, therefore, represented nominally a 100 ppm standard. Gas standards of lower concentration were made by dilution of the 100 ppm standard using a similar procedure. These standards were used immediately after preparation and were not retained for use on the following day.

Solution standards were made by weighing accurately known amounts of the components of interest and dissolving them in a known volume of pentane.

### A.6.4 Concentration factors

Desorbed compounds from the adsorbent tubes were concentrated into a 500 ml gas jar. For each particular test, therefore, the concentration factor would be the volume of emission passed through the tube divided by 500 ml. The volumes sampled for each tube varied from 1.5 cubic feet to 3.22 cubic feet during the complete test program giving a range of concentration factors from 85 to 181. Thus, a concentration for a particular component of 1 ppm in the gas jar sample would mean a concentration of about 10 ppb in the kiln emission, assuming a 100 percent collection efficiency, and subsequent desorption of the adsorbent.

Most of the extracted samples were concentrated into a 2 ml volume of solvent. The following example illustrates how the concentration factors were determined for various components detected. Assume that $CH_2Cl_2$ was detected at a concentration of 1 ppm in the solvent extract. This corresponds approximately to a weight of 2 μg of the compound in 2 ml of solvent. The molecular weight of $CH_2Cl_2$ is 85. Therefore, 2 μg of $CH_2Cl_2$ at 70°C, the temperature at which the emission sample was measured, occupies a volume of:

$$\frac{2}{85 \times 10^6} \times 24 \text{ litres, or } \frac{2}{85 \times 10^6} \times \frac{24}{28.3} \text{ cubic feet.}$$

For test WBA 1, for example, a volume of 142.81 scf was sampled. Thus, the concentration of $CH_2Cl_2$ in the kiln emission is:

$$\frac{2}{85 \times 10^6} \times \frac{24}{28.3} \times \frac{10^6}{142.81} \text{ ppm or } 0.14 \text{ ppb.}$$

The concentration factor is therefore $\frac{10^3}{0.14} = 7140$.

Factors were calculated for feed compounds of lowest and highest molecular weight.

### A.6.5 Sample chromatograms

Analysis for low molecular weight organohalides and noncombusted chlorinated organic compounds present in any collected samples was made using GC techniques only, by selecting appropriate GC parameters and using retention time data. No specific cleanup or separation procedures were performed in order to segregate components of interest from possible interfering compounds because, although GC profiles obtained were quite complex, very low concentrations of organic compounds were evident from the peak heights obtained for the attenuations used. Estimates of specific compound concentrations in waste burn samples were made by subtracting blank and baseline levels and comparing with a standard for that compound.

Waste feeds. GC-FID profiles for the three waste feed materials burned in this study are given in Figures A.7 to A.9. Identification of the main components in the respective waste feeds are presented in Tables 1, 2 and 3 in Section 5 of the report.

It was anticipated that the levels, if any, of uncombusted components in the stack emissions would be very low. Therefore GC-EC analysis was used to evaluate the organic solvent extracts of the various impinger samples from the sampling trains for the presence of any uncombusted components. Figures A.10 and A.11 represent GC-EC profiles for diluted waste feed material for WBB and WBC, respectively. WBB also contained approximately 50% o-chlorotoluene which has a weak response to the EC detector. Therefore, in this instance the solvent extracts were also analyzed by GC-FID in order to determine whether any uncombusted o-chlorotoluene was present.

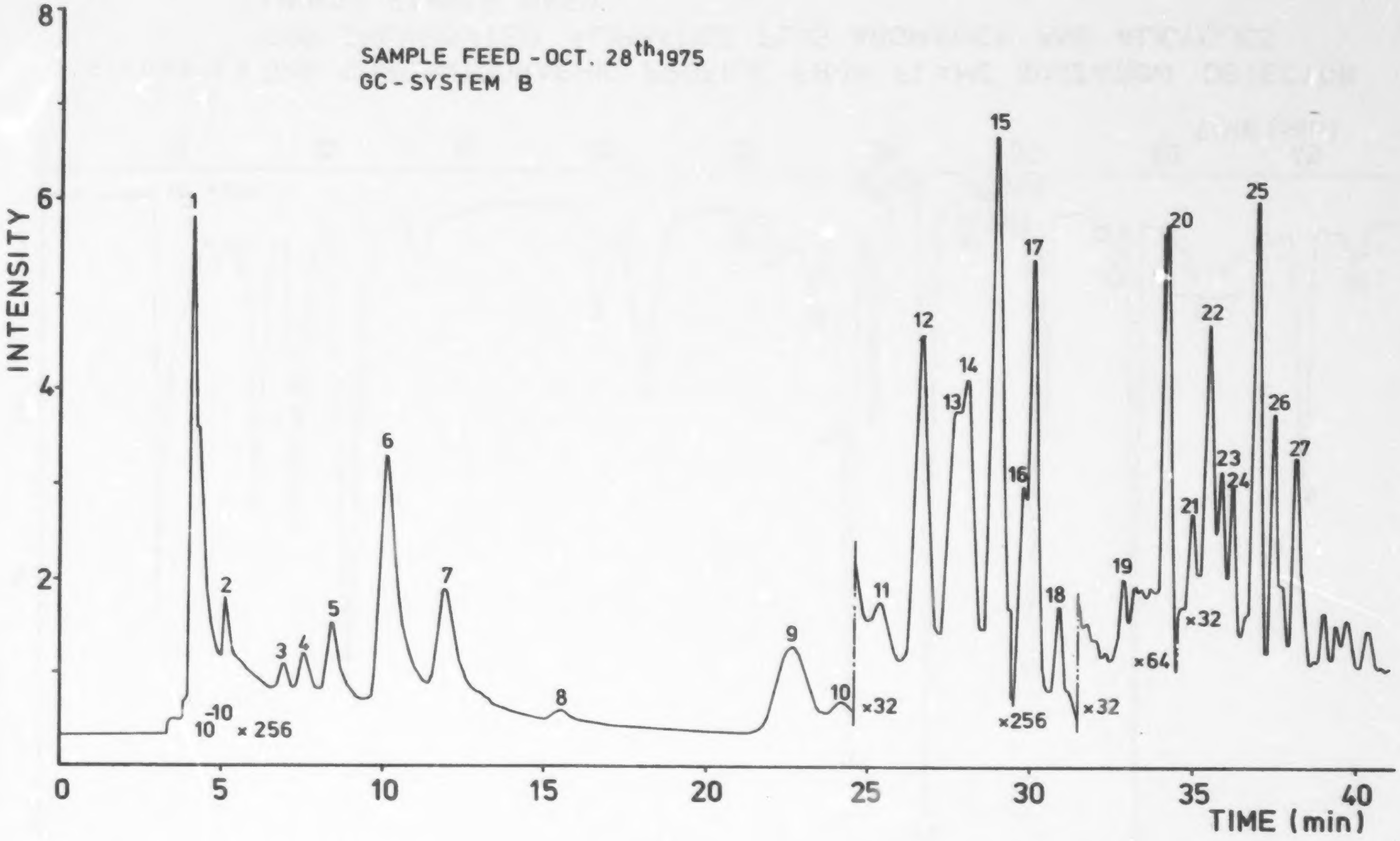


FIGURE A.7 GAS CHROMATOGRAPHIC PROFILE FROM FLAME IONIZATION DETECTOR FOR CHLORINATED ALIPHATICS (WBA) SAMPLE FEED

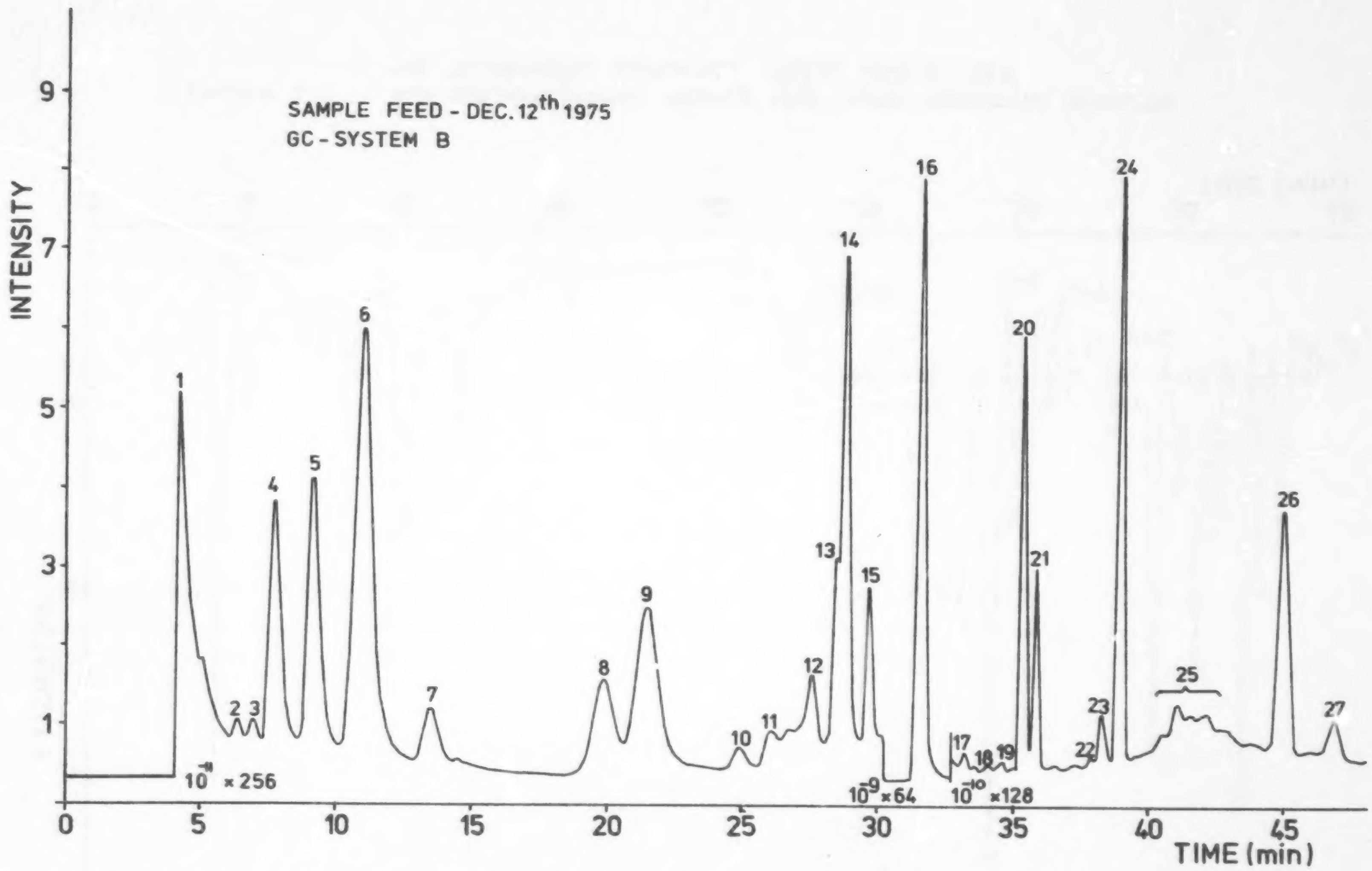


FIGURE A.8 GAS CHROMATOGRAPHIC PROFILE FROM FLAME IONIZATION DETECTOR FOR CHLORINATED ALIPHATICS PLUS AROMATICS AND ALICYCLICS (WBB) SAMPLE FEED

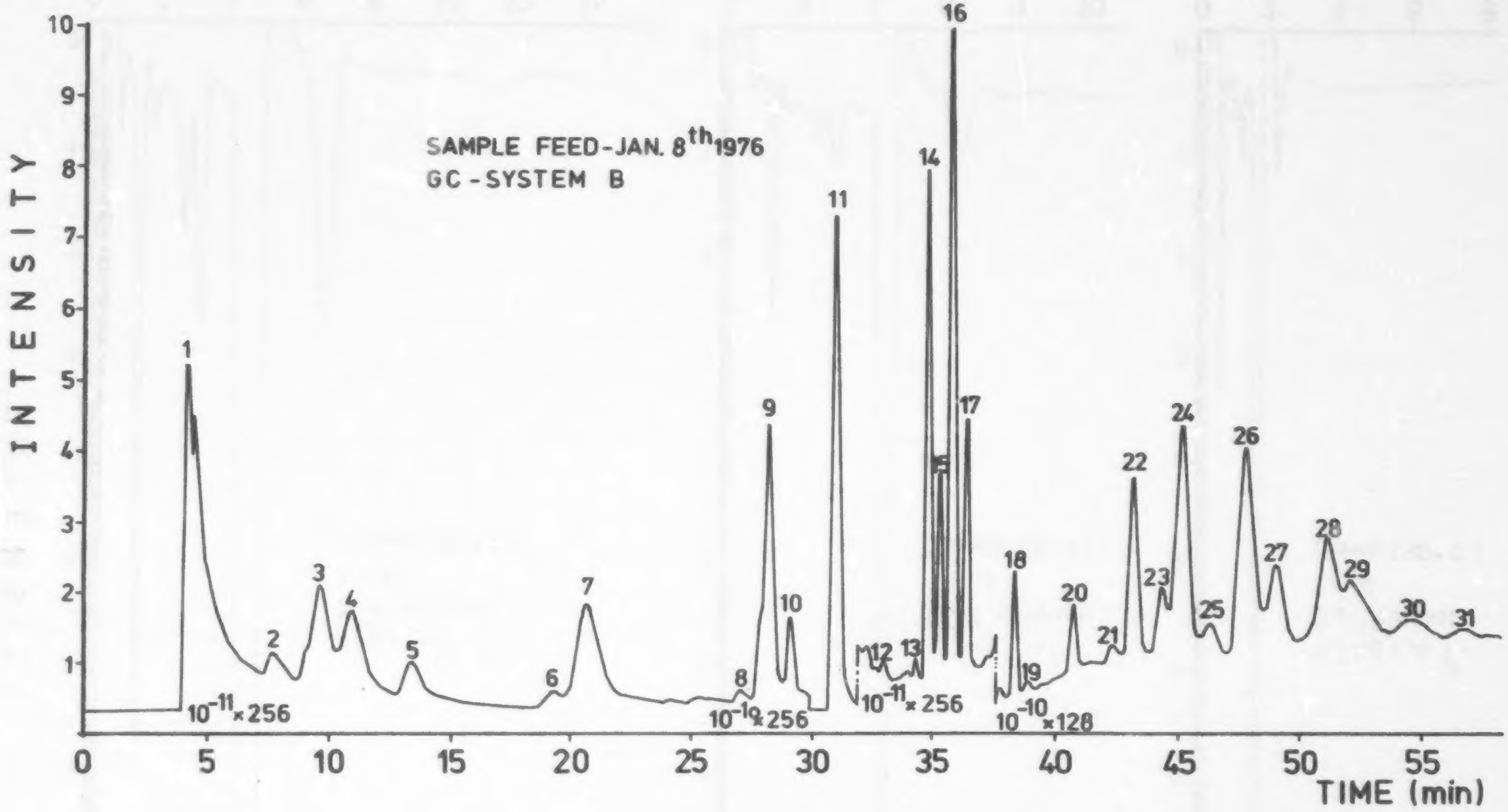


FIGURE A.9 GAS CHROMATOGRAPHIC PROFILE FROM FLAME IONIZATION DETECTOR FOR CHLORINATED ALIPHATICS PLUS AROMATICS, ALICYCLICS AND POLYCHLORINATED BIPHENYLS (WBC) SAMPLE FEED

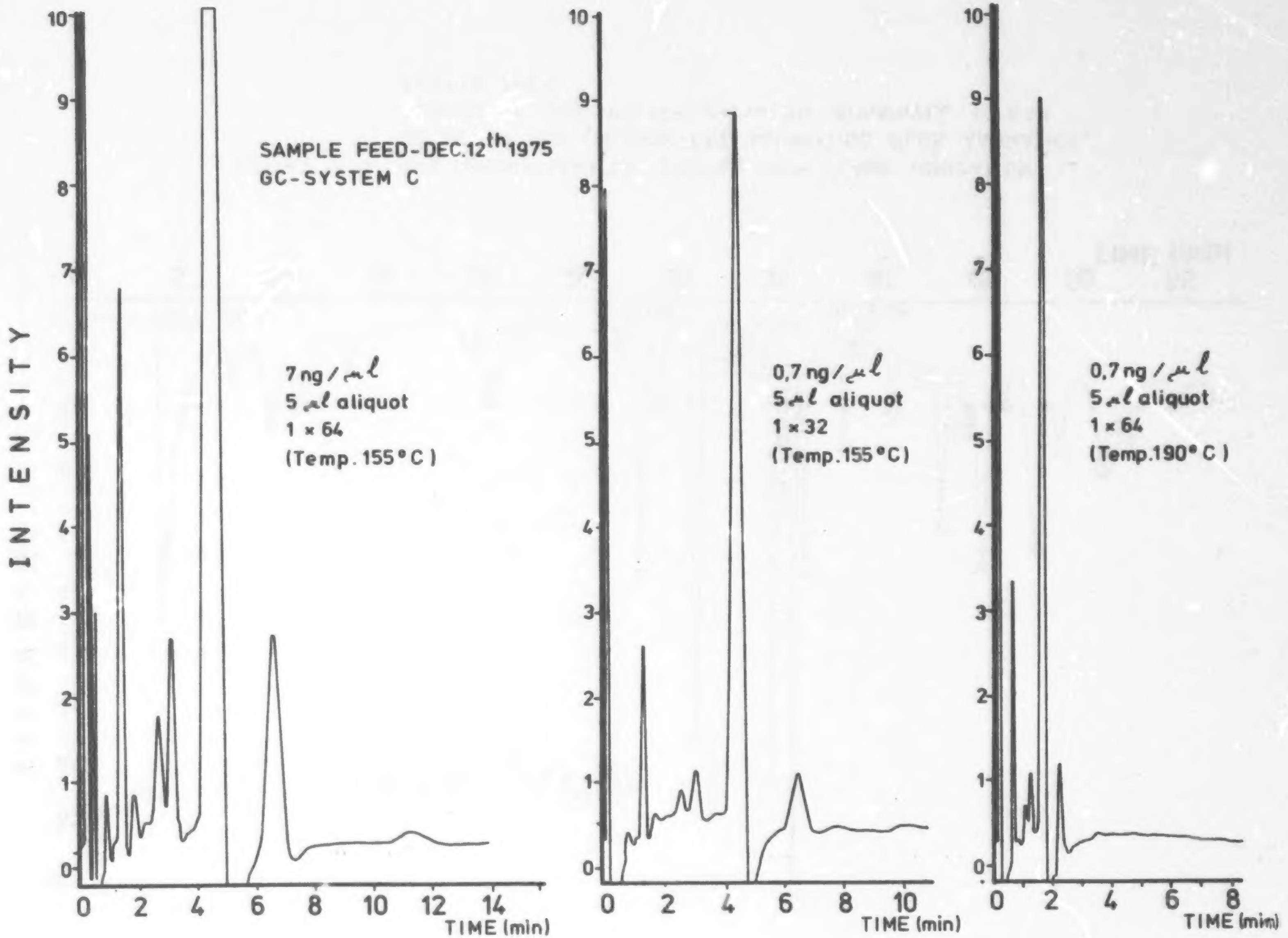


FIGURE A.10 GAS CHROMATOGRAPHIC PROFILES FROM ELECTRON CAPTURE DETECTOR FOR WBB SAMPLE FEED

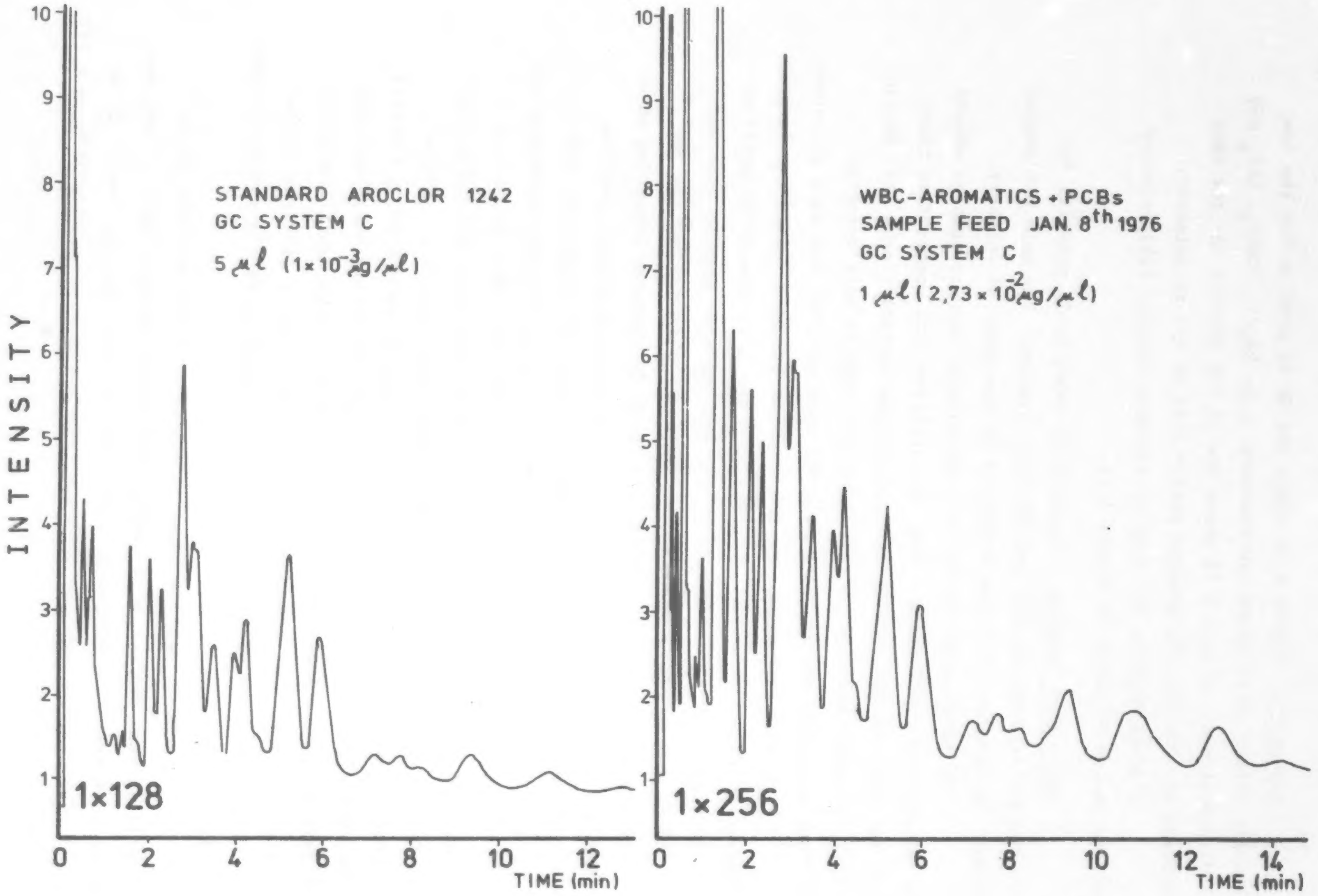


FIGURE A.11 GAS CHROMATOGRAPHIC PROFILES FROM ELECTRON CAPTURE DETECTOR FOR STANDARD AROCLOR 1242 AND SAMPLE FEED WBC

**Standards.** Figure A.12 shows the GC-EC profile for the low molecular weight chlorinated hydrocarbons, e.g. $CH_2Cl_2$, $CHCl_3$, $CCl_4$ and 1,2-dichlorethene. Figure A.13 shows the GC-FID profile for the same compounds to indicate the greater sensitivity of the EC detector.

A GC-EC profile for 5 ng of standard Aroclor 1242 injected into the column is shown in Figure A.11.

Waste Burn Samples. Figure A.12 shows GC-EC profiles for desorbed gas samples for BLB and WBC test samples. The main difference between the samples is in the intensity of the peaks of interest.

The GC-EC profiles for all the solvent extract samples showed the presence of small peaks. When the profiles were compared to those obtained from the BLA samples and the various control blanks (cf. Section A.6.3), no peaks peculiar to the waste burn samples were detected. BLB samples became contaminated with WBC feed material and were discarded.

In most instances, the EPA impinger extracts showed the largest response to the EC detector. Figures A.14 and A.15 show GC-EC profiles for the organic solvent extracts of the EPA impinger samples obtained for BLA-T3 and WBC-T3, respectively. Profiles obtained for the two samples are quite similar. There is a large EC response occurring as an unresolved peak in the early portion of the chromatographic profile. This limited the sample size that could be used for injection, and restricted the use of high sensitivity settings on the gas chromatograph.

It is normal practice when analysing for PCB's to perform cleanup and separation procedures in order to segregate the PCB's from interfering components and thus facilitate their analysis. Such a cleanup and separation procedure was performed on WBC-T3 using Florisil adsorbent (27) in order to determine whether the early unresolved peak (Figure A.15) could be removed. After cleanup, it was possible to use a larger aliquot for injection and higher sensitivity settings on the chromatograph. The GC-EC profile of the cleaned up WBC-T3 sample is shown in Figure A.16.

The GC-EC profile shown in Figure A.16 was obtained on an organic solvent extract of a sample that should contain PCB's if any were present in the kiln emissions. The profile shows the presence of a few small peaks. When compared with the Standard Aroclor profile (Figure A.11),

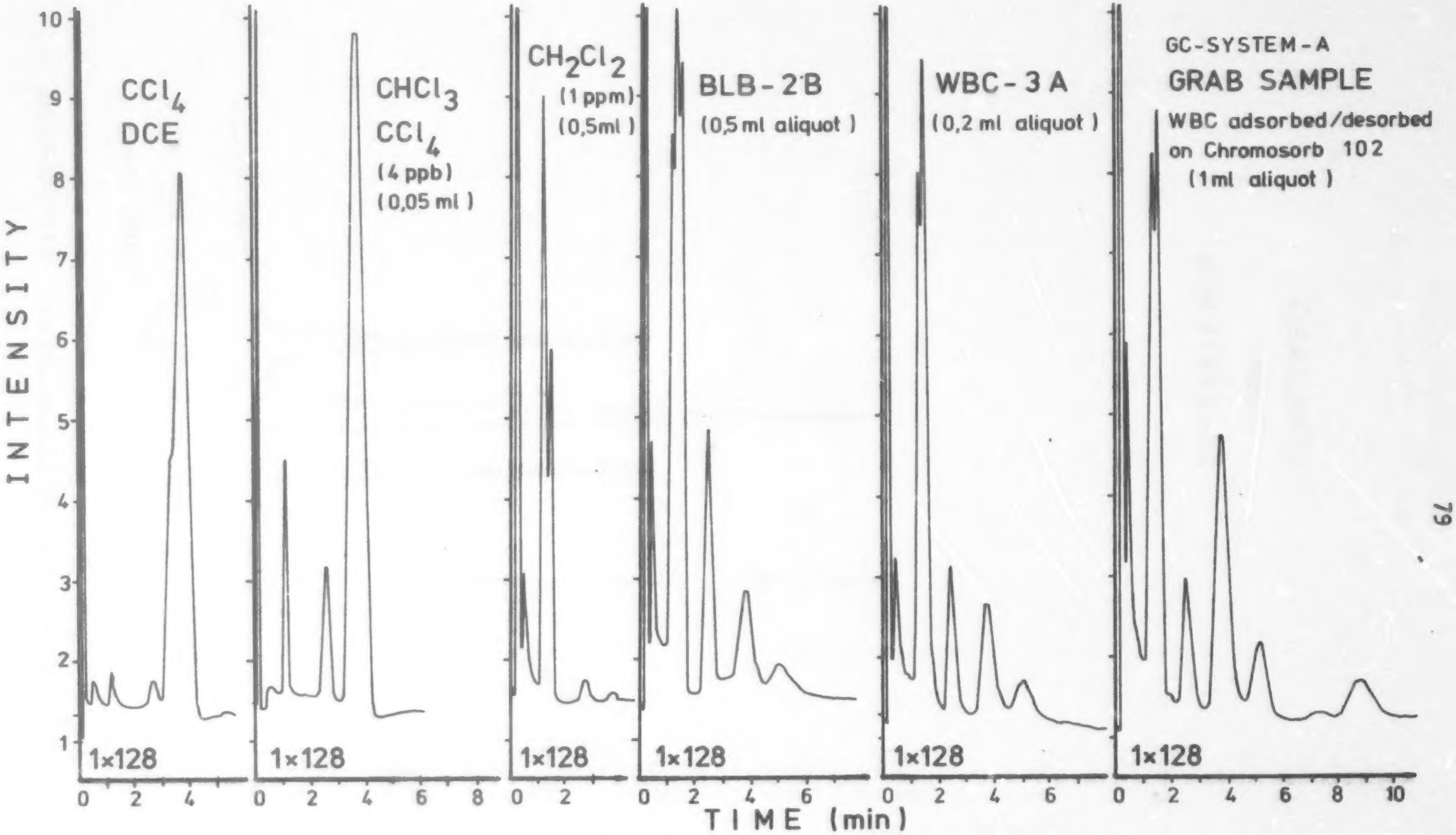


FIGURE A.12 GAS CHROMATOGRAPHIC PROFILES FROM ELECTRON CAPTURE DETECTOR FOR LOW MOLECULAR WEIGHT CHLORINATED HYDROCARBONS AND FOR BLB AND WBC TEST SAMPLES

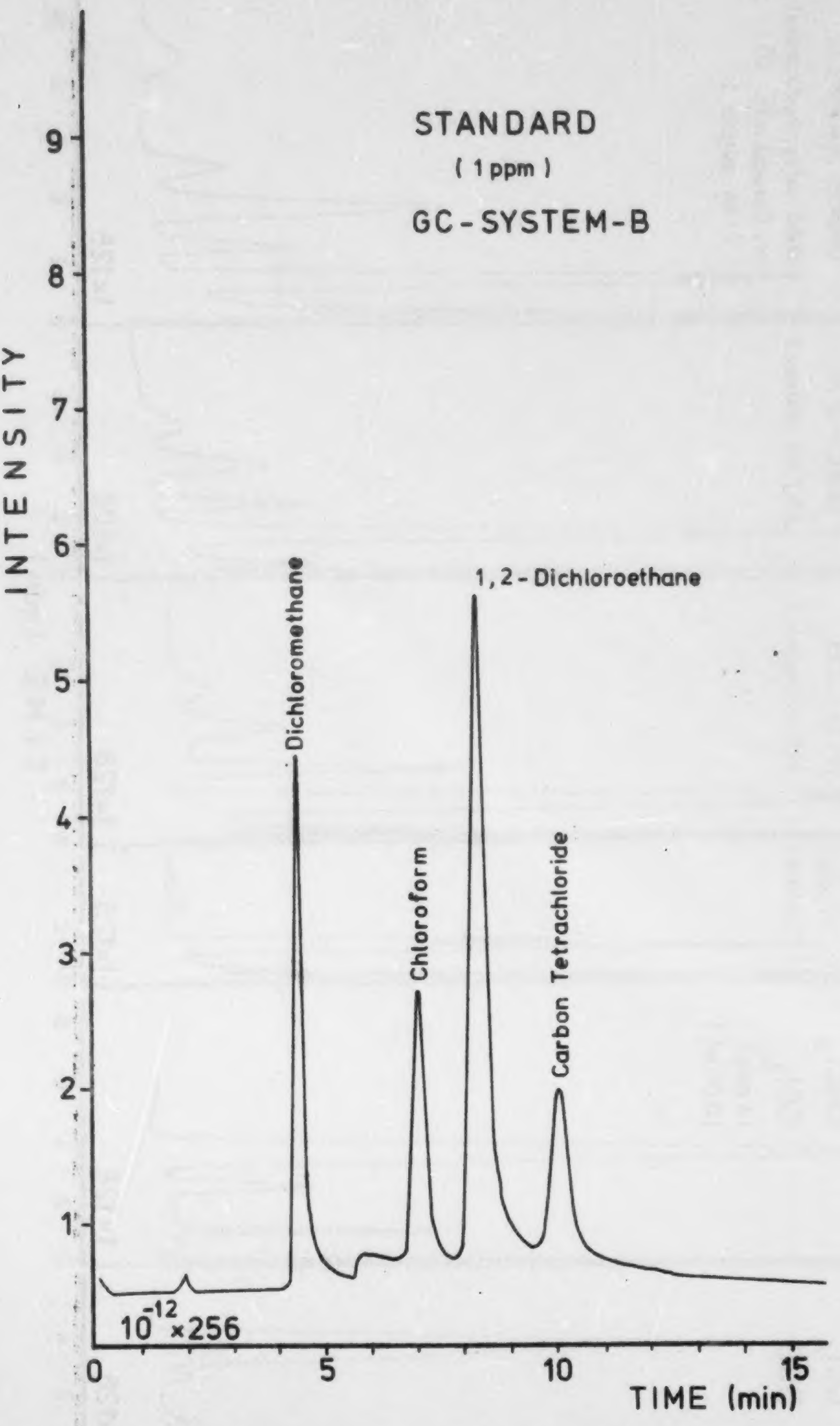


FIGURE A.13 GAS CHROMATOGRAPHIC PROFILE FROM FLAME IONIZATION DETECTOR FOR LOW MOLECULAR WEIGHT HYDROCARBONS

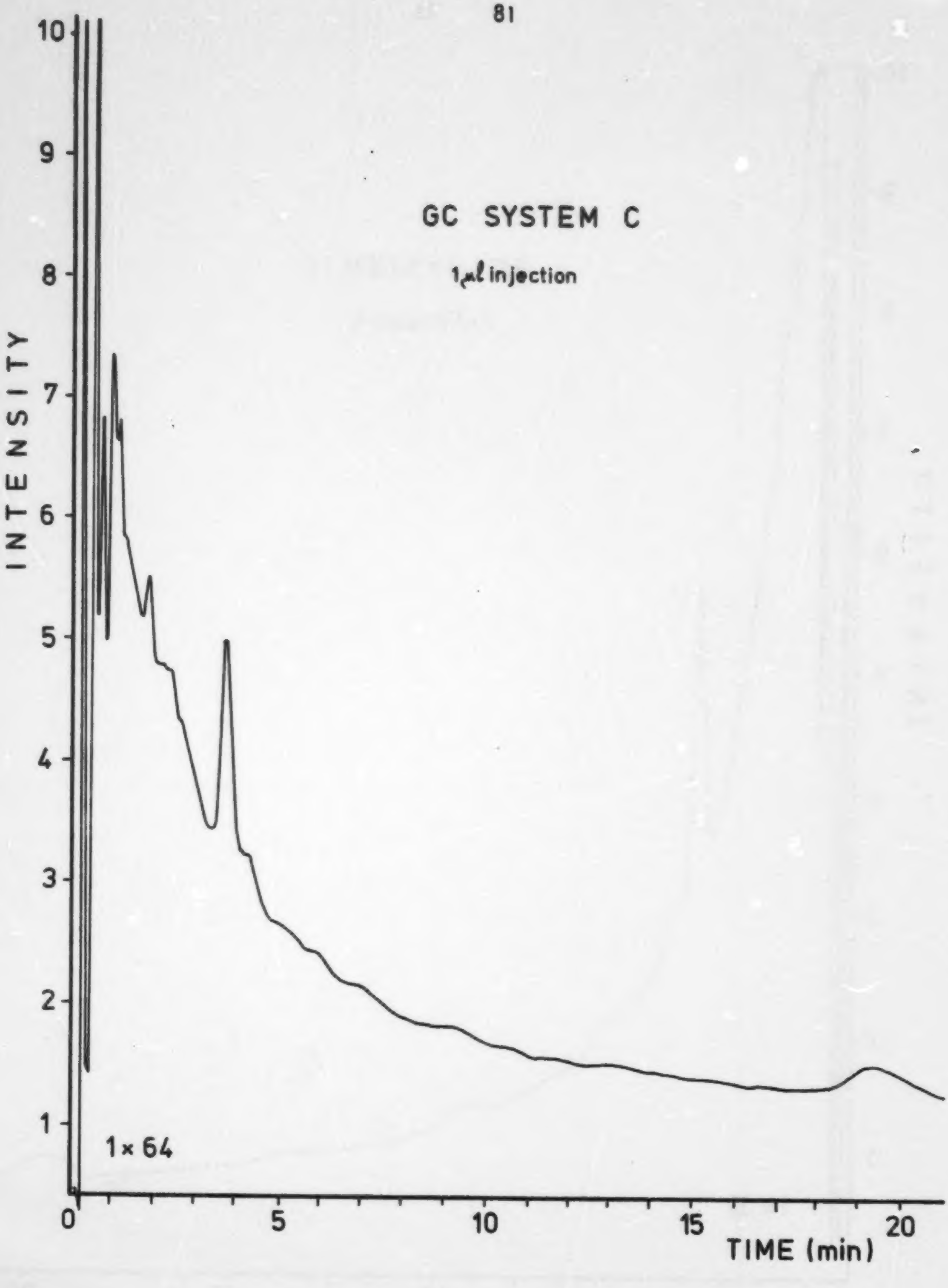


FIGURE A.14 GAS CHROMATOGRAPHIC PROFILE FROM ELECTRON CAPTURE DETECTOR FOR IMPINGER EXTRACT FROM BLA TEST 3

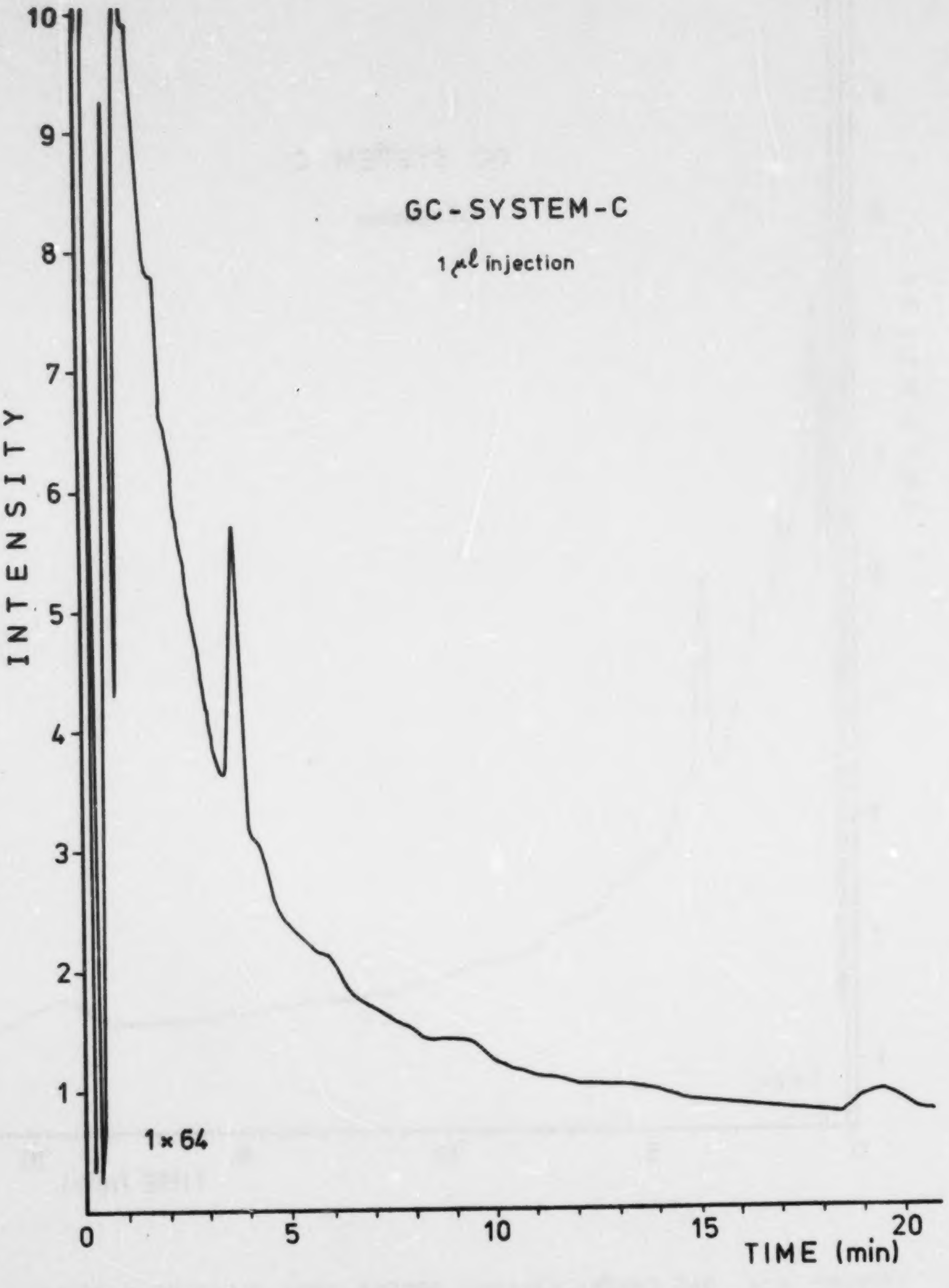


FIGURE A.15 GAS CHROMATOGRAPHIC PROFILE FROM ELECTRON CAPTURE DETECTOR FOR IMPINGER EXTRACT FROM WBC-TEST 3

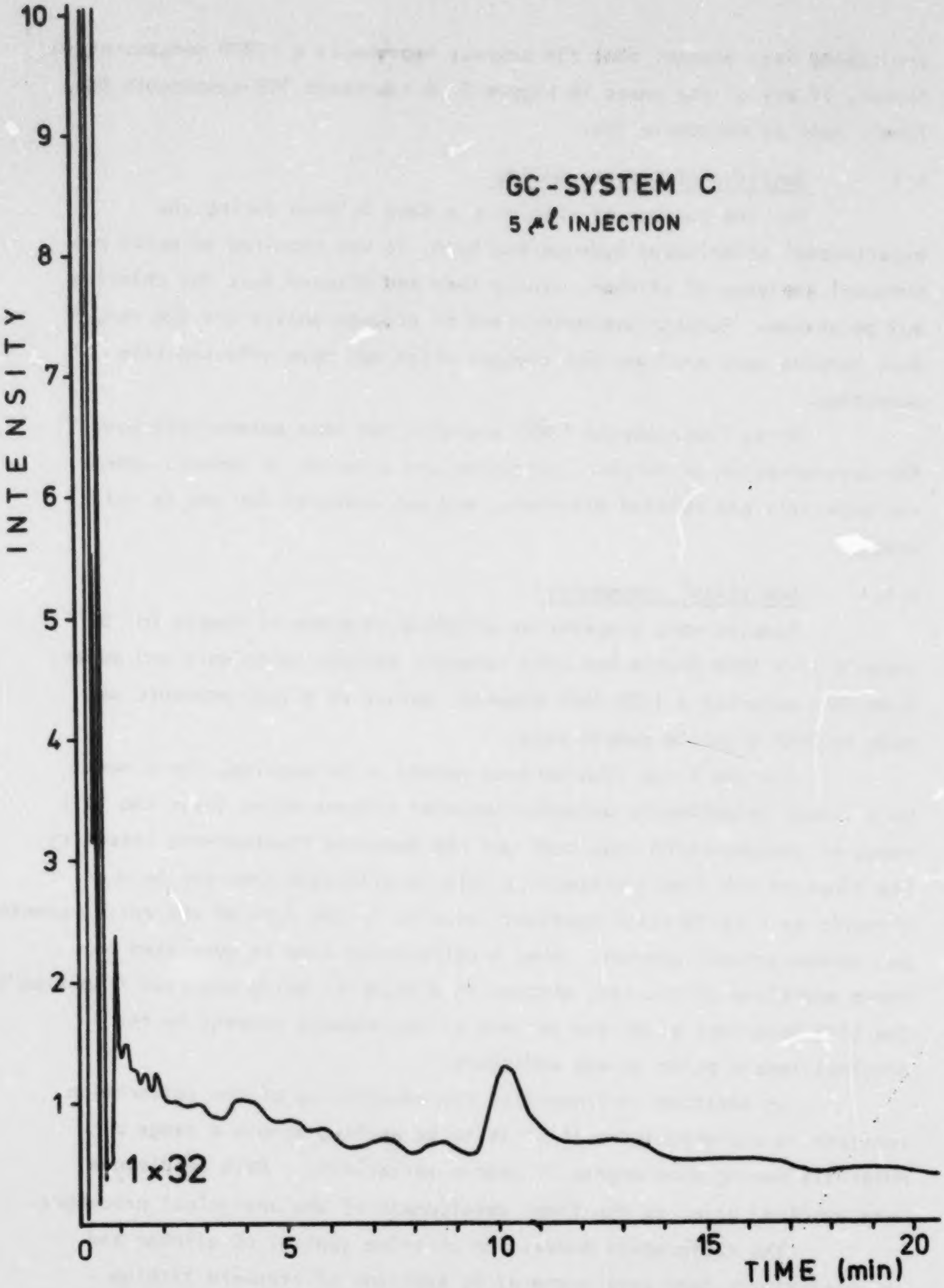


FIGURE A.16 GAS CHROMATOGRAPHIC PROFILE FROM ELECTRON CAPTURE DETECTOR FOR IMPINGER EXTRACT FROM WBC TEST 3 AFTER CLEANUP AND SEPARATION

and taking into account that the extract represents a >7000 concentration factor, if any of the peaks in Figure A.16 represent PCB components the levels must be extremely low.

## A.7 Analysis of Process Solids

For the purpose of obtaining a mass balance during the experimental chlorinated hydrocarbon burn, it was required to carry out chemical analyses of clinker, slurry feed and discard dust for chlorine and potassium. Sulphur was determined on process solids and the return dust samples were analyzed for changes which may have affected kiln operation.

X-ray fluorescence (XRF) analysis has been extensively used for determination of sulphur, potassium and chlorine in cement, cement raw materials and related materials, and was selected for use in this study.

### A.7.1 Analytical procedures

Samples were prepared by grinding 10 grams of sample for 90 seconds in a SPEX Shatterbox with tungsten carbide containers and pucks. From this material a 1.25 inch diameter pellet at 8 tons pressure was made in SPEX aluminum sample caps.

For the X-ray fluorescence method to be applied, there must be a linear relationship between elemental concentration (over the full range of concentration required) and the measured fluorescence intensity. The slope of the line representing this relationship then can be used directly as a calibration constant, usually in the form of the ratio, counts per second:percent element. When a calibration line is generated by known additions of the test element to a material being analyzed ("spiking"), the line intercept gives the percent of the element present in the original sample prior to any additions.

In addition to linearity, reproducibility of the calibration constant is a prerequisite if it is to be applied across a range of materials having some degree of matrix variability. Both conditions were examined prior to the final development of the analytical procedure.

The calibration curves for chlorine content of clinker and raw meal-slurry feed were prepared by addition of standard lithium chloride in alcohol solution to samples of these materials. Dust samples were analyzed by the standard Volhard method for calibration of the chlorine curve and the standard gravimetric method of precipitation with barium for calibration of the sulphur curve (Table A.8). For calibration of curves for sulphur in clinker and raw meal/slurry feed, determinations were made on a Leco Induction Furnace Model 523CS with Leco Automatic Titrator Model 517 (Table A.9). For calibration of the potassium curve, all potassium results, as well as those for sodium, were obtained from analyses on a Perkin-Elmer Model 460 Atomic Absorption Spectrophotometer in the flame emission mode (Table A.10).

Examination of these samples yielded linear calibration relationships between X-ray fluorescence count rates and percent element. The least squares computations for each set of data gave the slopes, intercepts and regression (correlation) coefficients listed in Table A.11.

TABLE A.8. GRAVIMETRIC DUST ANALYSES

| Dust Type | Date | % Cl | % $SO_3$ |
|---|---|---|---|
| Discard | 19/10/75 | 2.00 | - |
| " | 11/11/75 | 2.08 | 3.17 |
| " | 31/11/75 | 5.97 | 2.36 |
| " | 4/12/75 | 2.89 | 6.53 |
| " | 5/12/75 | 7.11 | 12.12 |
| " | 6/12/75 | 4.69 | 7.27 |
| " | 7/12/75 | 6.18 | 6.90 |
| " | 5/ 1/76 | 4.71 | 5.08 |
| " | 6/ 1/76 | 3.72 | 4.23 |
| " | 9/ 1/76 | 4.43 | 4.18 |
| " | 14/ 1/76 | 0.46 | 4.65 |
| " | 16/ 1/76 | 0.90 | 4.32 |
| Return | 5/12/75 | 2.11 | 7.35 |
| " | 13/12/75 | 4.34 | 4.22 |
| " | 1/ 1/76 | 2.10 | 4.99 |
| " | 18/ 1/76 | 1.00 | 5.66 |

## TABLE A.9. RESULTS FROM LECO INDUCTION FURNACE ANALYSES

| Material | Date | % $SO_3$ (Total S as) |
|---|---|---|
| Clinker | 19/10/75 | 0.93 |
| " | 21/10/75 | 1.34 |
| " | 23/10/75 | 0.75 |
| " | 31/10/75 | 0.30 |
| " | 1/11/75 | 0.16 |
| " | 5/11/75 | 0.66 |
| " | 8/12/75 | 0.93 |
| " | 31/12/75 | 1.39 |
| " | 1/ 1/76 | 1.43 |
| " | 11/ 1/76 | 1.04 |
| " | 20/ 1/76 | 1.42 |
| Slurry Feed | 13/10/75 | 0.45 |
| " | 20/10/75 | 0.42 |
| " | 27/10/75 | 0.41 |
| " | 9/11/75 | 0.45 |
| " | 6/12/75 | 0.52 |
| " | 9/12/75 | 0.48 |
| " | 13/12/75 | 0.60 |
| " | 14/12/75 | 0.55 |
| " | 31/12/75 | 0.43 |
| " | 3/ 1/76 | 0.47 |
| " | 8/ 1/76 | 0.46 |
| " | 21/ 1/76 | 0.47 |

## TABLE A.10. RESULTS FROM ATOMIC ABSORPTION ANALYSES

| Material | Date | % $K_2O$ | % $Na_2O$ |
|---|---|---|---|
| Discard Dust | 11/11/75 | 6.36 | 0.32 |
| " | 31/11/75 | 10.30 | 0.39 |
| " | 4/12/75 | 7.14 | 0.36 |
| " | 6/12/75 | 8.23 | 0.44 |
| " | 7/12/75 | 9.96 | 0.45 |
| " | 5/ 1/76 | 8.12 | 0.43 |
| " | 6/ 1/76 | 6.43 | 0.34 |
| " | 9/ 1/76 | 7.94 | 0.39 |
| " | 14/ 1/76 | 4.84 | 0.35 |
| " | 16/ 1/76 | 4.18 | 0.34 |
| Return Dust | 5/12/75 | 7.79 | 0.42 |
| " | 13/12/75 | 5.54 | 0.41 |
| " | 1/ 1/76 | 6.02 | 0.41 |
| Clinker | 19/10/75 | 1.32 | 0.23 |
| " | 21/10/75 | 1.61 | 0.25 |
| " | 23/10/75 | 1.00 | 0.20 |
| " | 31/10/75 | 0.54 | 0.21 |
| " | 1/11/75 | 0.40 | 0.21 |
| " | 5/11/75 | 1.01 | 0.21 |
| " | 8/12/75 | 0.64 | 0.20 |
| " | 31/12/75 | 1.18 | 0.21 |
| " | 1/ 1/76 | 1.31 | 0.24 |
| " | 11/ 1/76 | 1.10 | 0.22 |
| " | 20/ 1/76 | 1.45 | 0.26 |
| Slurry Feed | 13/10/75 | 0.93 | 0.19 |
| " | 20/10/75 | 0.93 | 0.22 |
| " | 27/10/75 | 0.89 | 0.18 |
| " | 9/11/75 | 0.88 | 0.20 |
| " | 6/12/75 | 0.91 | 0.19 |
| " | 9/12/75 | 0.90 | 0.22 |
| " | 31/12/75 | 0.90 | 0.18 |
| " | 3/ 1/76 | 0.91 | 0.22 |
| " | 8/ 1/76 | 0.93 | 0.19 |
| " | 21/ 1/76 | 0.94 | 0.22 |

## TABLE A.11. LEAST SQUARES DATA FOR CALIBRATION LINES

| Material | Element | Correlation Coefficient | Slope | Intercept |
|---|---|---|---|---|
| Raw Meal + Slurry Feed | Potassium (as $K_2O$) | 0.9172 | 27128 | -0.01 |
| | Chlorine | 0.9995 | 5260 | 0.060 |
| | Sulphur (as $SO_3$) | 0.9913 | 739 | 0.27 |
| Clinker | Potassium (as $K_2O$) | 0.9829 | 24980 | -0.01 |
| | Chlorine | 0.9999 | 4781 | 0.011 |
| | Sulphur (as $SO_3$) | 0.9917 | 400 | -0.23 |
| Dust | Potassium (as $K_2O$) | | 3166 | -0.12 |
| | Chlorine | 0.9893 | 1927 | -0.14 |
| | Sulphur (as $SO_3$) | 0.9548 | 278 | -0.10 |

### A.8 Determination of Heat Value, Chlorine Content and Sulphur Content in No. 6 Fuel

The heat value was determined using standard methods on a Parr Calorimeter Model 1241 equipped with Parr oxygen bomb Model 1108. Sulphur was determined using the standard barium precipitation method on the washings from the bomb. Where chlorine content was required, the washings were analyzed for chlorine by the standard Volhard method.

### A.9 Determination of Heat Value and Chlorine Content in Chlorinated Hydrocarbons

The heat value was determined on a Parr calorimeter model 1241 equipped with Parr oxygen bomb model 1108 following standard operating procedures for determining heat value of oil. Due to the corrosive nature of the combustion products, it is recommended that the chlorinated materials be diluted with standard oil. It has been found that, while corrosion of the interior of the bomb is extensive, burning these materials without dilution gives similar results. Time between weighing and igniting is extremely important due to the volatile nature of some of these compounds.

After igniting and determining the heat value of the chlorinated material, the interior of the bomb is thoroughly washed with distilled water into a volumetric flask. Aliquots of the proper size for the chlorine content expected were taken. Nitric acid is added to allow a more distinct end point, and the chlorine is determined by the standard Volhard titration.

## REFERENCES

A.1 Ontario Ministry of the Environment, Source Testing Code. January, 1973.

A.2 Standard Reference Methods for Source Testing: Measurement of Emissions of Particulates from Stationary Sources. Environmental Protection Service Report EPS 1-AP-74-1, Air Pollution Control Directorate, Environment Canada, February, 1974.

A.3 Pellizan, E.D., J.E. Bunch, and B.H. Carpenter. Env. Sci. Technology 9 (6), 552-560 (1975).

## APPENDIX B

## ANALYTICAL DATA, CALCULATION AND DETAILS OF EXPERIMENT ON THE SUSPENSION PREHEATER KILN

### B.1 Theoretical

The excellent article by Weber cited in the body of the report describes in detail the problem of alkali reduction in a suspension preheater kiln, and was used in preparing the following notes.

At material temperatures above 800°C in the rotary kiln, alkalies ($K_2O$ and $Na_2O$) are volatilized from the material being burned and are carried along with the exit gases to the kiln inlet. These condense at gas temperatures below 900°C. In part, they are recaptured by the material, particularly in the preheater, and are thus carried back to the sintering zone, so that an internal alkali cycle is established. The alkalies are in part also precipitated at the transition from the preheater to the kiln.

Coatings thus formed interfere with material and gas flows and, in the most severe cases, completely plug the system.

In preheater kilns, the raw meal is heated in the finely divided condition in the gas stream and these particles act as condensation nuclei for the alkalies. Between 81 and 97% of the $K_2O$ volatilized in the kiln is trapped in the preheater.

The greater the alkali cycle, and therefore the concentration of alkali in the gas, the more alkali will condense on the bottom ducts and cyclone stages. If the alkali is very volatile, accretions are likely to occur in the preheater. However, the alkali cycle can be reduced by the provision of a bypass, that is by drawing off a portion of the gas at the bottom of the preheater. (See Figure 3, Section 2 of the report.)

Of alkali which enters the kiln system with the raw meal, a proportion ($\varepsilon_1$) will be volatilized and the remaining ($1- \varepsilon_1$) will be discharged with the clinker. If the proportion of gas withdrawn through the bypass is V, then of the volatilized alkalies, the proportion $\varepsilon_1 \cdot V$ will be removed by the bypass. The remaining portion $\varepsilon_1$ $(1-V)$ will return with the feed, thereby giving rise to the internal cycle in the kiln.

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The alkali in the internal cycle has a different volatility $\varepsilon_2$ than alkali from the raw meal which has not yet been volatilized. By defining total alkali including raw meal alkali into the kiln by K, then the quantity of alkali from the cycle alone is K-1. Of this quantity, $(K-1)\cdot\varepsilon_2\cdot V$ is removed by the bypass.

Equilibrium is attained when the total quantity of alkali input with raw meal and fuel is equal to the quantity output by the bypass and retained with the clinker. This is most easily determined by considering only alkali in the cycle. Entering the cycle is the volatile raw meal alkali $= \varepsilon_1$; leaving the cycle are a proportion in the clinker $= (K-1)\cdot(1-\varepsilon_2)$ and a proportion through the bypass $= [\varepsilon_1 + (K-1)\ \varepsilon_2)]\cdot V$.

By setting the quantities input and output from the cycle as equal, the equation may be solved to determine the amount of gas the bypass must remove to keep the alkali cycle from becoming excessive.

## B.2 Experience at St. Lawrence Cement

At St. Lawrence Cement, samples are taken of the material between the Stage IV cyclone and the kiln inlet (see Figure 3), this material being called, not quite appropriately, "Stage IV dust". From experience at St. Lawrence Cement, it was known that a chloride content of 2.5% chlorine in this material (natural basis) is excessive. The quantity of gas required to be withdrawn by the bypass to maintain lower chloride levels was calculated on the assumption that the chloride volatilities were $\varepsilon_1 = 0.99$ and $\varepsilon_2 = 1.0$ (completely volatile). These quantities are given in Table B.1.

While the bypass was designed to remove the quantities of gas required for the program, attempts to reach this level resulted in excessive emissions of particulate matter from the bypass precipitator. These were attributed to excessive gas flows. To alleviate this problem, measures to increase cooling water and decrease the quantity of ambient air were undertaken, with limited success.

TABLE B.1. PERCENT BYPASS GAS REQUIRED TO MAINTAIN CHLORIDE LEVELS

| Chloride addition relative to clinker | % $K_2O$ in clinker | Bypass percent required to maintain Stage IV Cl at: 1.56% or 2.0% nat. ign. | 2.0% or 2.56% nat. ign. | 2.5% or 3.2% nat. ign. |
|---|---|---|---|---|
| 0 | 1.31 | 2.1 | 1.6 | 1.3 |
| 0.05 | 1.24 | 4.6 | 3.6 | 2.9 |
| 0.10 | 1.18 | 7.1 | 5.5 | 4.4 |
| 0.15 | 1.11 | 9.6 | 7.5 | 6.0 |
| 0.20 | 1.04 | 12.1 | 9.4 | 7.0 |
| 0.30 | 0.91 | 17.1 | 11.7 | 10.6 |
| 0.40 | 0.77 | 22.2 | 17.2 | 13.8 |

### B.3 Equation of Approximated Time for Equilibrium

It was essential to the success of the program to determine the time required to attain the equilibrium state. To obtain an approximation of the time required, and realizing that it is only an approximation since retention time in kiln and absorption phenomena influence this time, the following approach was taken:

$$\frac{dQ}{dt} = Cl_{RM} - Cl_{clinker} - Cl_{bypass}$$

where:

$\frac{dQ}{dt}$ = change in quantity with time (pounds/minute)

$Cl_{RM}$ = chlorine/time in with raw meal (pounds/minute)

$Cl_{clinker}$ = chlorine/time out with clinker (pounds/minute)

$Cl_{bypass}$ = chlorine/time out through bypass (pounds/minute)

$Cl_{RM}$ and $Cl_{clinker}$ are approximately constant, hence they can be combined as:

$$I_{cl} = Cl_{RM} - Cl_{clinker}$$

and $Cl_{bypass} = VQ(t)$

where:

$Q(t)$ = quantity in transition chamber at time (t) in pounds
$V$ = bypass valve proportion.

Then:

$$\frac{dQ}{dt} = I_{cl} - VQ(t)$$

Solving for time gives:

$$t = \frac{\ln [I_{cl} - VQ(t)]}{V} \Bigg|_{Q_F}^{Q_0} \quad \text{minutes.}$$

Since $\ln 0 = \infty$, $Q_F$ must be taken as a very small distance from the true equilibrium.

The sampling sequence at Stage IV was planned from this model.

## B.4 Sampling and Analytical Methods

Analytical methods were those described in Appendix A. Samples of clinker, raw meal feed, bypass precipitator dust and conditioning tower dust were taken at two hour intervals. These were then blended into 24-hour composite samples. On the basis of the calculation in Section B.3, samples were taken from Stage IV at 3 to 10 minute intervals when attempting to start the chlorinated burn. These latter samples were analyzed individually.

## B.5 Discussion

In both cases described, the bypass was operated to withdraw 9 percent of the gases from the preheater tower. This was the maximum attainable due to the emission rate of particulate matter. On the first attempt to burn chlorinated hydrocarbons, the quantity to yield 0.24 percent chlorine relative to clinker was fed starting at 09:38, June 3, 1975. Plugging of the duct between the kiln and the conditioning tower caused a bypass shutdown on June 5, 1975. It was not possible to maintain feed of chlorinated material to the kiln unless the bypass was functioning. On June 10, 1975 a second and similar attempt was started at 11:20. The bypass again failed due to accretion on the duct on June 13, 1975. On the second attempt, sampling of Stage IV material was continued for a longer period on the basis of the first set of results.

It was realized with the failure that major revisions to the bypass system would be required to continue this experiment on the suspension preheater kiln.

## B.6 Analytical Results

Analytical results are given in Tables B.2 through B.4. The raw meal feeds showed a gradual increase in both the content of chlorine and $K_2O$. The results from the clinker analysis (Table B.3) showed that the burning of chlorinated hydrocarbons resulted in a reduction in the $K_2O$ content (June 3-5, 1975 and June 10-12, 1975).

The results of the analyses from Stage IV dusts (Table B.4) show that the chlorinated hydrocarbons were destroyed in the burning process. Chloride content of these samples increased while burning chlorinated wastes. This finding could not have resulted without breakdown of the hydrocarbons since the raw material is at too high temperature at this position in the preheater for the chlorinated hydrocarbons to condense upon it. By the methods described in Section B.3, the approximate time to equilibrium was calculated to be about 90 minutes. It was also expected that an additional time of approximately 20 minutes would be required to travel through the kiln. The actual curve is less steep and equilibrium is reached in about four hours. For the June 3, 1975 burn, the curve was extrapolated to the calculated equilibrium (Figure B.1). On June 10, 1975 samples were taken for a longer period. Although there are points above the calculated curve (Figure B.2), the data from June 11, 1975 show that equilibrium was reached; the higher values found indicate random sampling or analytical errors.

### TABLE B.2. RESULTS FROM ANALYSES OF DRY PROCESS KILN RAW FEEDS

| Date | % Cl | % $SO_3$ (Total S as) | % $K_2O$ |
|---|---|---|---|
| 30/5/75 | 0.067 | 0.60 | 0.92 |
| 31/5/75 | 0.069 | 0.60 | 0.95 |
| 1/6/75 | 0.073 | 0.60 | 0.93 |
| 2/6/75 | 0.071 | 0.60 | 0.93 |
| 3/6/75 | 0.074 | 0.60 | 0.93 |
| 4/6/75 | 0.082 | 0.60 | 0.95 |
| 5/6/75 | 0.079 | 0.60 | 0.96 |
| 6/6/75 | 0.094 | 0.62 | 0.98 |
| 7/6/75 | 0.087 | 0.60 | 0.97 |
| 8/6/75 | 0.093 | 0.60 | 0.97 |
| 9/6/75 | 0.088 | 0.58 | 0.97 |
| 10/6/75 | 0.084 | 0.60 | 0.95 |
| 11/6/75 | 0.092 | 0.60 | 0.98 |
| 12/6/75 | - | NO SAMPLE | - |
| 13/6/75 | 0.084 | 0.60 | 0.96 |
| 14/6/75 | 0.104 | 0.60 | 1.00 |
| 15/6/75 | 0.102 | 0.62 | 1.00 |

## TABLE B.3. RESULTS FROM ANALYSES OF DRY PROCESS KILN CLINKER

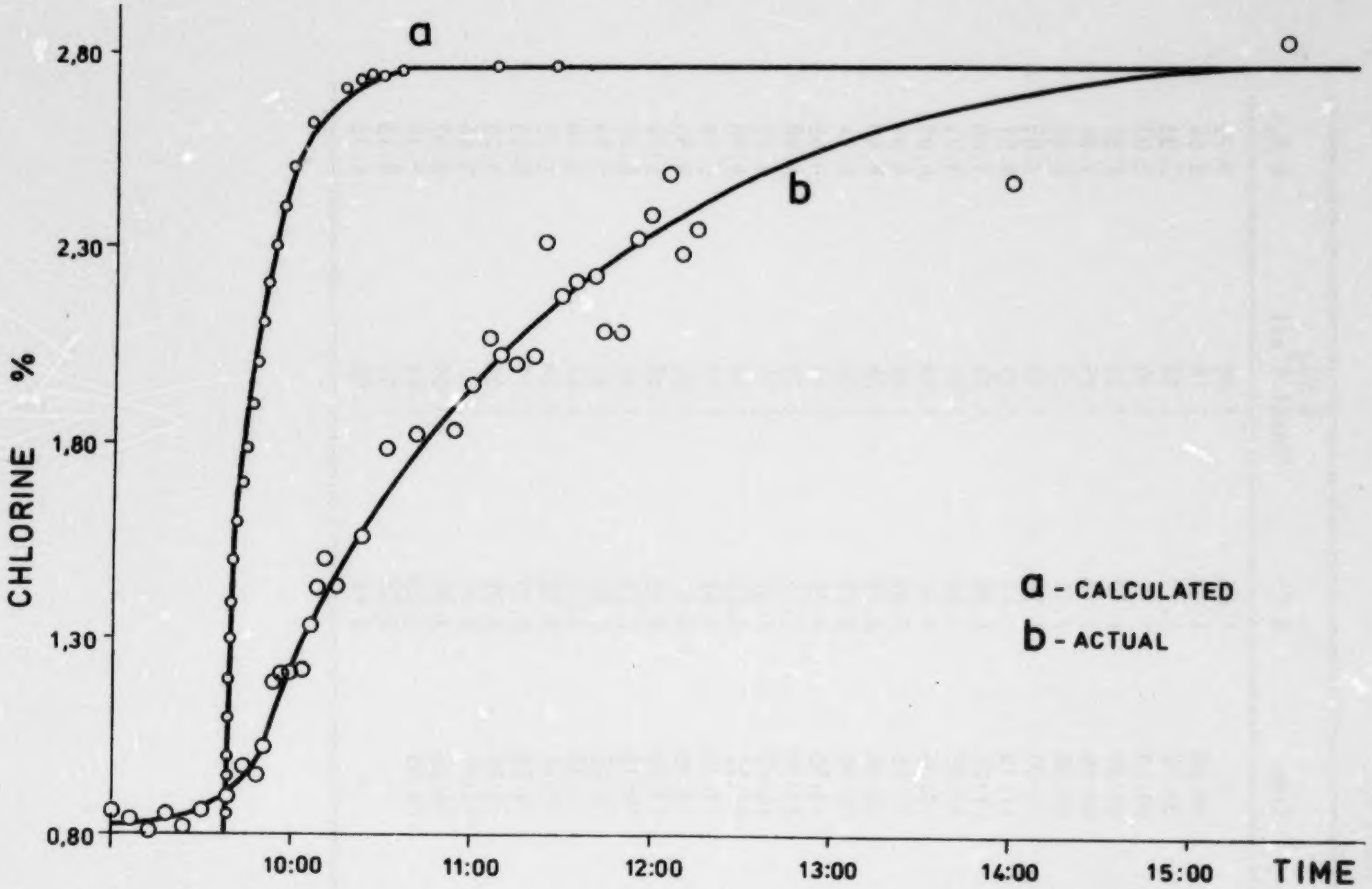
| Date | Time | % Cl | % $SO_2$ | % $K_2O$ |
|---|---|---|---|---|
| 30/5/75 | Average | 0.03 | 1.05 | 1.27 |
| 31/5/75 | " | 0.03 | 1.15 | 1.29 |
| 1/6/75 | " | 0.03 | 1.15 | 1.31 |
| 2/6/75 | " | 0.21 | 1.16 | 1,30 |
| 3/6/75 | " | 0.03 | 1.10 | 1.24 |
| 4/6/75 | " | 0.05 | 1.19 | 1.30 |
| 5/6/75 | " | 0.04 | 1.23 | 1.33 |
| 6/6/75 | " | 0.04 | 1.34 | 1.44 |
| 7/6/75 | " | 0.07 | 1.33 | 1.48 |
| 8/6/75 | " | 0.05 | 1.31 | 1.43 |
| 9/6/75 | " | 0.06 | 1.50 | 1.63 |
| 10/6/75 | " | 0.04 | 1.22 | 1.29 |
| 10/6/75 | 12:00 | 0.06 | 1.38 | 1.25 |
| 10/6/75 | 14:00 | 0.04 | 1.00 | 0.97 |
| 10/6/75 | 16:00 | 0.04 | 1.07 | 0.87 |
| 10/6/75 | 18:00 | 0.05 | 1.30 | 1.10 |
| 10/6/75 | 20:00 | 0.05 | 1.03 | 0.96 |
| 10/6/75 | 22:00 | 0.05 | 1.11 | 1.05 |
| 11/6/75 | Average | 0.06 | 1.29 | 1.24 |
| 11/6/75 | 00:00 | 0.04 | 1.18 | 1.27 |
| 11/6/75 | 02:00 | 0.06 | 1.36 | 1.25 |
| 11/6/75 | 04:00 | 0.07 | 0.98 | 1.00 |
| 11/6/75 | 06:00 | 0.06 | 0.96 | 0.99 |
| 11/6/75 | 08:00 | 0.06 | 1.10 | 1.10 |
| 11/6/75 | 10:00 | 0.05 | 1.08 | 1.08 |
| 11/6/75 | 14:00 | 0.05 | 1.18 | 1.15 |
| 11/6/75 | 16:00 | 0.05 | 1.08 | 1.13 |
| 11/6/75 | 18:00 | 0.06 | 1.12 | 1.14 |
| 11/6/75 | 20:00 | 0.05 | 1.23 | 1.21 |
| 11/6/75 | 22:00 | 0.05 | 1.01 | 1.06 |
| 12/6/75 | Average | 0.07 | 1.28 | 1.29 |
| 12/6/75 | 00:00 | 0.07 | 1.07 | 1.15 |
| 12/6/75 | 02:00 | 0.05 | 1.12 | 1.16 |
| 12/6/75 | 04:00 | 0.05 | 1.11 | 1.15 |
| 12/6/75 | 06:00 | 0.05 | 1.10 | 1.16 |
| 12/6/75 | 08:00 | 0.05 | 1.11 | 1.18 |
| 12/6/75 | 10:00 | 0.10 | 1.25 | 1.36 |
| 12/6/75 | 12:00 | 0.05 | 1.11 | 1.15 |
| 12/6/75 | 14:00 | 0.06 | 1.23 | 1.28 |
| 12/6/75 | 16:00 | 0.05 | 1.11 | 1.17 |
| 12/6/75 | 18:00 | 0.05 | 1.14 | 1.18 |
| 13/6/75 | Average | 0.05 | 1.29 | 1.40 |
| 14/6/75 | " | 0.05 | 1.40 | 1.52 |
| 15/6/75 | " | 0.04 | 1.35 | 1.41 |

## TABLE B.4. RESULTS FROM ANALYSES OF STAGE IV DUSTS

| Date | Time | % Cl | % $SO_3$ (Total S as) | % $K_2O$ |
|---|---|---|---|---|
| 30/ 5/76 | - | 0.67 | 1.14 | 1.77 |
| 2/ 6/75 | - | 0.82 | 1.30 | 2.26 |
| 3/ 6/75 | 09:00 | 0.86 | 1.23 | 2.11 |
| 3/ 6/75 | 09:06 | 0.84 | 1.25 | 2.03 |
| 3/ 6/75 | 09:12 | 0.81 | 1.19 | 2.03 |
| 3/ 6/75 | 09:18 | 0.85 | 1.22 | 2.14 |
| 3/ 6/75 | 09:24 | 0.82 | 1.18 | 2.06 |
| 3/ 6/75 | 09:30 | 0.86 | 1.30 | 2.17 |
| 3/ 6/75 | 09:38 | 0.90 | 1.34 | 2.15 |
| 3/ 6/75 | 09:44 | 0.97 | 1.32 | 2.21 |
| 3/ 6/75 | 09:47 | 0.96 | 1.35 | 2.38 |
| 3/ 6/75 | 09:50 | 1.02 | 1.38 | 2.39 |
| 3/ 6/75 | 09:53 | 1.20 | 1.29 | 2.37 |
| 3/ 6/75 | 09:56 | 1.21 | 1.31 | 2.42 |
| 3/ 6/75 | 09:59 | 1.21 | 1.34 | 2.51 |
| 3/ 6/75 | 10:02 | 1.22 | 1.30 | 2.55 |
| 3/ 6/75 | 10:05 | 1.34 | 1.46 | 2.68 |
| 3/ 6/75 | 10:08 | 1.44 | 1.38 | 2.66 |
| 3/ 6/75 | 10:11 | 1.51 | 1.52 | 2.95 |
| 3/ 6/75 | 10:14 | 1.44 | 1.29 | 2.91 |
| 3/ 6/75 | 10:23 | 1.56 | 1.41 | 2.94 |
| 3/ 6/75 | 10:32 | 1.79 | 1.37 | 3.38 |
| 3/ 6/75 | 10:41 | 1.83 | 1.34 | 3.43 |
| 3/ 6/75 | 10:54 | 1.85 | 1.32 | 3.35 |
| 3/ 6/75 | 10:59 | 1.95 | 1.46 | 3.74 |
| 3/ 6/75 | 11:04 | 2.08 | 1.59 | 3.85 |
| 3/ 6/75 | 11:09 | 2.03 | 1.35 | 3.72 |
| 3/ 6/75 | 11:14 | 2.00 | 1.39 | 3.66 |
| 3/ 6/75 | 11:19 | 2.03 | 1.41 | 3.70 |
| 3/ 6/75 | 11:24 | 2.30 | 1.47 | 4.15 |
| 3/ 6/75 | 11:29 | 2.17 | 1.36 | 3.93 |
| 3/ 6/75 | 11:34 | 2.21 | 1.37 | 4.04 |
| 3/ 6/75 | 11:39 | 2.22 | 1.43 | 4.00 |
| 3/ 6/75 | 11:44 | 2.29 | 1.51 | 4.18 |
| 3/ 6/75 | 11:49 | 2.29 | 1.57 | 4.11 |
| 3/ 6/75 | 11:54 | 2.32 | 1.66 | 4.24 |
| 3/ 6/75 | 11:59 | 2.38 | 1.47 | 4.36 |
| 3/ 6/75 | 12:04 | 2.49 | 1.51 | 4.45 |
| 3/ 6/75 | 12:09 | 2.28 | 1.46 | 4.12 |
| 3/ 6/75 | 12:14 | 2.34 | 1.44 | 4.21 |
| 3/ 6/75 | 14:00 | 2.47 | 1.45 | 4.44 |
| 3/ 6/75 | 15:30 | 2.84 | 1.58 | 5.07 |
| 4/ 6/75 | 09:00 | 1.92 | 1.42 | 4.17 |
| 4/ 6/75 | 14:00 | 1.59 | 1.28 | 3.48 |
| 5/ 6/75 | - | 0.97 | 1.44 | 2.54 |
| 6/ 6/75 | - | 1.14 | 1.17 | 2.71 |

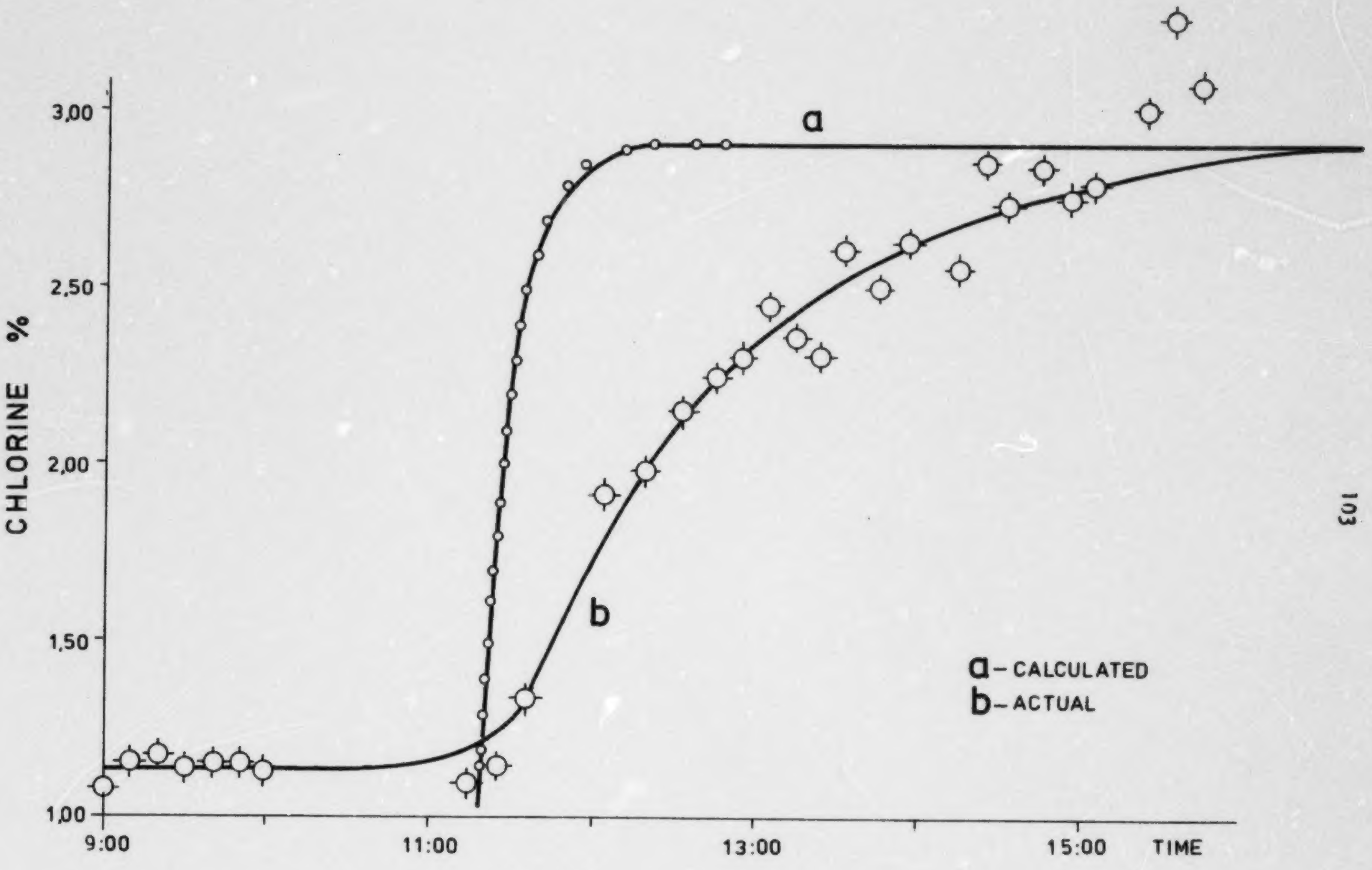
TABLE B.4. (Cont'd)

| Date | Time | % Cl | % $SO_3$ (Total S as) | % $K_2O$ |
|---|---|---|---|---|
| 9/ 6/75 | - | 1.66 | 1.20 | 3.79 |
| 10/ 6/75 | 09:00 | 1.09 | 1.18 | 2.64 |
| 10/ 6/75 | 09:10 | 1.17 | 1.22 | 2.93 |
| 10/ 6/75 | 09:20 | 1.19 | 1.36 | 3.07 |
| 10/ 6/75 | 09:30 | 1.15 | 1.39 | 2.92 |
| 10/ 6/75 | 09:40 | 1.16 | 1.29 | 3.01 |
| 10/ 6/75 | 09:50 | 1.16 | 1.27 | 2.99 |
| 10/ 6/75 | 10:00 | 1.14 | 1.29 | 2.95 |
| 10/ 6/75 | 11:15 | 1.11 | 1.29 | 2.91 |
| 10/ 6/75 | 11:25 | 1.20 | 1.34 | 3.04 |
| 10/ 6/75 | 11:35 | 1.46 | 1.41 | 3.22 |
| 10/ 6/75 | 12:05 | 1.91 | 1.49 | 4.02 |
| 10/ 6/75 | 12:25 | 1.99 | 1.46 | 4.07 |
| 10/ 6/75 | 12:35 | 2.15 | 1.64 | 4.50 |
| 10/ 6/75 | 12:45 | 2.25 | 1.59 | 4.54 |
| 10/ 6/75 | 12:55 | 2.31 | 1.66 | 4.65 |
| 10/ 6/75 | 13:05 | 2.45 | 1.79 | 4.98 |
| 10/ 6/75 | 13:15 | 2.37 | 1.71 | 4.75 |
| 10/ 6/75 | 13:25 | 2.32 | 1.47 | 4.48 |
| 10/ 6/75 | 13:35 | 2.62 | 1.67 | 5.10 |
| 10/ 6/75 | 13:45 | 2.51 | 1.54 | 4.83 |
| 10/ 6/75 | 13:55 | 2.63 | 1.69 | 5.12 |
| 10/ 6/75 | 14:15 | 2.57 | 1.69 | 5.02 |
| 10/ 6/75 | 14:25 | 2.87 | 1.81 | 5.53 |
| 10/ 6/75 | 14:35 | 2.74 | 1.67 | 5.18 |
| 10/ 6/75 | 14:45 | 2.85 | 1.70 | 5.35 |
| 10/ 6/75 | 14:55 | 2.77 | 1.77 | 5.23 |
| 10/ 6/75 | 15:05 | 2.79 | 1.52 | 5.23 |
| 10/ 6/75 | 15:25 | 3.02 | 2.41 | 5.66 |
| 10/ 6/75 | 15:35 | 3.28 | 1.59 | 6.07 |
| 10/ 6/75 | 15:45 | 3.09 | 1.62 | 5.78 |
| 11/ 6/75 | - | 2.58 | 1.51 | 5.23 |
| 12/ 6/75 | - | 2.42 | 1.49 | 5.13 |



CHLORINE LEVEL IN STAGE IV 3 /6/1975

FIGURE B.1



CHLORINE LEVEL IN STAGE IV 10 / 6 / 1975

FIGURE B.2

# APPENDIX C

## RESULTS AND CALCULATIONS FOR WET PROCESS SYSTEM

### C.1 Mass Balance Experimentation

### C.1.1 Results of analyses of process materials

Analyses of process materials for the mass balance were carried out at the St. Lawrence Cement Co. plant. Analytical results are given in Tables C.1 to C.6.

### C.1.2 Calculation of material balances

A daily record of production and material consumption is given in Table C.7 for the period October 7, 1975 to January 21, 1976. Production was disrupted during this period by a kiln shutdown for the removal of a kiln ring.

The program was further disrupted by formation of a ring, not requiring kiln shutdown, but time to reduce the quantity of aromatic plus complex chlorinated hydrocarbon in the tank and difficulty in scheduling deliveries. From the daily composite analysis of each material for each element, and the total daily quantity of each material, daily elemental quantities (as pounds or tons per 25 hour period) were determined by the relationship:

$$X_{ij} = M_{ij} \times \frac{C_{ij}}{100}$$

where

$X_{ij}$ = total daily weight of element x in material i on day j
$C_{ij}$ = concentration of element x in the composite sample material i on day j.

These data were then used to form the separate individual elemental balance accounts given in Tables C.8 and C.9. Due to process fluctuations and the very low concentrations in the case of chlorine, little significance should be attached to individual daily balance results, except as they indicate the responsiveness of the system to major changes in input of chlorinated hydrocarbons. Significant assessment of the

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balance is available by considering prolonged periods of plant operation. Summary balances for this purpose are given in the body of this report (see Section 5.4, Tables 8 and 9).

Materials entering the mass balance calculations (see Figure 1, Section 2) were slurry feed, No. 6 fuel oil and chlorinated hydrocarbon materials as input streams with clinker and discard dust forming the output streams. The return dust is returned almost immediately to the system and does not form a part of the mass balance.

TABLE C.1. RESULTS FROM ANALYSES OF CLINKER SAMPLES

| Date | % Cl | % $SO_3$ | % $K_2O$ |
|---|---|---|---|
| 7/10/75 | 0.033 | 0.88 | 1.13 |
| 8/10/75 | 0.032 | 0.79 | 1.12 |
| 9/10/75 | 0.034 | 0.86 | 1.14 |
| 10/10/75 | 0.042 | 0.62 | 0.88 |
| 11/10/75 | 0.032 | 0.93 | 1.27 |
| 12/10/75 | 0.029 | 0.80 | 1.08 |
| 13/10/75 | 0.030 | 0.80 | 1.09 |
| 14/10/75 | 0.031 | 0.86 | 1.15 |
| 15/10/75 | 0.031 | 1.27 | 1.47 |
| 16/10/75 | 0.031 | 0.90 | 1.16 |
| 17/10/75 | 0.035 | 1.11 | 1.31 |
| 18/10/75 | 0.029 | 0.99 | 1.24 |
| 19/10/75 | 0.032 | 0.97 | 1.21 |
| 20/10/75 | 0.042 | 1.03 | 1.28 |
| 21/10/75 | 0.030 | 1.32 | 1.51 |
| 22/10/75 | 0.029 | 0.99 | 1.28 |
| 23/10/75 | 0.030 | 0.77 | 1.06 |
| 24/10/75 | 0.030 | 0.92 | 1.20 |
| 25/10/75 | 0.029 | 0.59 | 0.83 |
| 26/10/75 | 0.031 | 1.06 | 1.24 |
| 27/10/75 | 0.031 | 0.82 | 1.00 |
| 28/10/75 | 0.034 | 1.16 | 1.31 |
| 29/10/75 | 0.032 | 1.27 | 1.37 |
| 30/10/75 | 0.039 | 0.88 | 0.96 |
| 31/10/75 | 0.034 | 0.34 | 0.49 |
| 1/11/75 | 0.039 | 0.18 | 0.36 |
| 2/11/75 | - | NO SAMPLE | - |
| 3/11/75 | 0.032 | 0.26 | 0.48 |
| 4/11/75 | 0.028 | 0.30 | 0.56 |
| 5/11/75 | 0.031 | 0.64 | 1.00 |
| 6/11/75 | 0.031 | 0.70 | 1.18 |
| 7/11/75 | 0.037 | 0.71 | 1.20 |
| 8/11/75 | 0.029 | 0.68 | 1.15 |
| 9/11/75 | 0.035 | 0.72 | 1.19 |
| 2/12/75 | 0.031 | 1.13 | 0.94 |
| 3/12/75 | 0.029 | 1.39 | 1.28 |
| 4/12/75 | 0.034 | 1.02 | 1.01 |
| 5/12/75 | 0.033 | 1.23 | 1.16 |
| 6/12/75 | 0.029 | 1.18 | 0.90 |
| 7/12/75 | 0.028 | 1.18 | 0.84 |
| 8/12/75 | 0.038 | 0.91 | 0.74 |
| 9/12/75 | 0.040 | 0.71 | 0.56 |
| 10/12/75 | 0.034 | 0.47 | 0.36 |
| 11/12/75 | 0.035 | 0.70 | 0.48 |
| 12/12/75 | 0.032 | 0.92 | 0.54 |
| 13/12/75 | 0.032 | 0.75 | 0.39 |
| 14/12/75 | 0.031 | 0.73 | 0.48 |

TABLE C.1 (CONT'D)

| Date | % Cl | % $SO_3$ | % $K_2O$ |
|---|---|---|---|
| 31/12/75 | 0.029 | 1.40 | 1.20 |
| 1/ 1/76 | 0.029 | 1.48 | 1.34 |
| 2/ 1/76 | 0.029 | 1.49 | 1.37 |
| 3/ 1/76 | 0.033 | 1.12 | 0.77 |
| 4/ 1/76 | 0.030 | 1.68 | 1.42 |
| 5/ 1/76 | 0.035 | 1.14 | 0.78 |
| 6/ 1/76 | 0.031 | 0.70 | 0.58 |
| 7/ 1/76 | 0.029 | 1.14 | 1.26 |
| 8/ 1/76 | 0.030 | 0.88 | 0.83 |
| 9/ 1/76 | 0.028 | 0.46 | 0.46 |
| 10/ 1/76 | 0.028 | 0.91 | 1.05 |
| 11/ 1/76 | 0.030 | 0.92 | 1.12 |
| 12/ 1/76 | 0.030 | 0.94 | 1.15 |
| 13/ 1/76 | 0.029 | 1.13 | 1.35 |
| 14/ 1/76 | 0.030 | 1.14 | 1.28 |
| 15/ 1/76 | 0.029 | 1.12 | 1.22 |
| 16/ 1/76 | 0.030 | 1.38 | 1.45 |
| 17/ 1/76 | 0.037 | 1.36 | 1.42 |
| 18/ 1/76 | 0.028 | 1.20 | 1.27 |
| 19/ 1/76 | 0.028 | 1.06 | 1.15 |
| 20/ 1/76 | 0.029 | 1.42 | 1.46 |
| 21/ 1/76 | 0.029 | 0.94 | 1.12 |

## TABLE C.2 RESULTS FROM ANALYSES OF SLURRY FEED SAMPLES

| Date | % Cl | % $SO_3$ (Total S as) | % $K_2O$ |
|---|---|---|---|
| 7/10/75 | 0.080 | 0.48 | 0.92 |
| 8/10/75 | 0.056 | 0.48 | 0.91 |
| 9/10/75 | 0.052 | 0.45 | 0.91 |
| 10/10/75 | 0.058 | 0.46 | 0.91 |
| 11/10/75 | 0.060 | 0.46 | 0.92 |
| 12/10/75 | 0.068 | 0.45 | 0.92 |
| 13/10/75 | 0.050 | 0.50 | 0.93 |
| 14/10/75 | 0.044 | 0.44 | 0.92 |
| 15/10/75 | 0.046 | 0.44 | 0.93 |
| 16/10/75 | 0.043 | 0.43 | 0.93 |
| 17/10/75 | 0.051 | 0.43 | 0.93 |
| 18/10/75 | 0.055 | 0.43 | 0.93 |
| 19/10/75 | 0.046 | 0.44 | 0.93 |
| 20/10/75 | 0.043 | 0.42 | 0.93 |
| 21/10/75 | 0.038 | 0.41 | 0.92 |
| 22/10/75 | 0.040 | 0.40 | 0.93 |
| 23/10/75 | 0.040 | 0.40 | 0.93 |
| 24/10/75 | 0.050 | 0.40 | 0.93 |
| 25/10/75 | 0.043 | 0.41 | 0.92 |
| 26/10/75 | 0.055 | 0.42 | 0.93 |
| 27/10/75 | 0.042 | 0.43 | 0.91 |
| 28/10/75 | 0.047 | 0.41 | 0.92 |
| 29/10/75 | 0.055 | 0.43 | 0.93 |
| 30/10/75 | - | NO SAMPLE | - |
| 31/10/75 | 0.050 | 0.42 | 0.91 |
| 1/11/75 | 0.047 | 0.42 | 0.91 |
| 2/11/75 | 0.043 | 0.42 | 0.92 |
| 3/11/75 | 0.043 | 0.43 | 0.93 |
| 4/11/75 | 0.044 | 0.44 | 0.92 |
| 5/11/75 | 0.042 | 0.41 | 0.93 |
| 6/11/75 | 0.042 | 0.43 | 0.92 |
| 7/11/75 | 0.044 | 0.41 | 0.92 |
| 8/11/75 | 0.042 | 0.40 | 0.91 |
| 9/11/75 | 0.050 | 0.43 | 0.94 |
| 2/12/75 | 0.046 | 0.48 | 0.90 |
| 3/12/75 | 0.042 | 0.48 | 0.90 |
| 4/12/75 | 0.041 | 0.47 | 0.89 |
| 5/12/75 | 0.040 | 0.52 | 0.91 |
| 6/12/75 | 0.040 | 0.51 | 0.90 |
| 7/12/75 | 0.052 | 0.53 | 0.91 |
| 8/12/75 | 0.041 | 0.51 | 0.91 |
| 9/12/75 | 0.040 | 0.51 | 0.89 |

TABLE C.2 (CONT'D)

| Date | % Cl | % $SO_3$ (Total S as) | % $K_2O$ |
|---|---|---|---|
| 10/12/75 | 0.041 | 0.54 | 0.91 |
| 11/12/75 | 0.039 | 0.52 | 0.91 |
| 12/12/75 | 0.050 | 0.55 | 0.91 |
| 13/12/75 | 0.042 | 0.58 | 0.90 |
| 14/12/75 | 0.048 | 0.54 | 0.91 |
| 31/12/75 | 0.059 | 0.48 | 0.90 |
| 1/ 1/76 | 0.042 | 0.46 | 0.91 |
| 2/ 1/76 | 0.045 | 0.46 | 0.92 |
| 3/ 1/76 | 0.043 | 0.46 | 0.91 |
| 4/ 1/76 | 0.046 | 0.46 | 0.92 |
| 5/ 1/76 | 0.038 | 0.46 | 0.91 |
| 6/ 1/76 | 0.038 | 0.46 | 0.91 |
| 7/ 1/76 | 0.048 | 0.47 | 0.91 |
| 8/ 1/76 | 0.039 | 0.46 | 0.89 |
| 9/ 1/76 | 0.048 | 0.45 | 0.92 |
| 10/ 1/76 | 0.048 | 0.46 | 0.91 |
| 11/ 1/76 | 0.048 | 0.44 | 0.91 |
| 12/ 1/76 | 0.040 | 0.44 | 0.91 |
| 13/ 1/76 | 0.041 | 0.44 | 0.92 |
| 14/ 1/76 | 0.044 | 0.46 | 0.91 |
| 15/ 1/76 | 0.042 | 0.47 | 0.91 |
| 16/ 1/76 | 0.048 | 0.50 | 0.91 |
| 17/ 1/76 | 0.041 | 0.47 | 0.90 |
| 18/ 1/76 | 0.054 | 0.46 | 0.91 |
| 19/ 1/76 | 0.039 | 0.44 | 0.91 |
| 20/ 1/76 | 0.040 | 0.43 | 0.91 |
| 21/ 1/76 | 0.041 | 0.43 | 0.92 |

## TABLE C.3. RESULTS FROM ANALYSES OF DISCARD DUST

| Date | % CL | % $SO_3$ (Total S as) | % $K_2O$ |
|---|---|---|---|
| 7/10/75 | 0.99 | 7.09 | 7.37 |
| 8/10/75 | 1.01 | 7.22 | 7.45 |
| 9/10/75 | 0.89 | 7.28 | 7.34 |
| 10/10/75 | 0.96 | 7.48 | 7.66 |
| 11/10/75 | 0.96 | 7.39 | 7.48 |
| 12/10/75 | 1.35 | 7.59 | 8.26 |
| 13/10/75 | 2.51 | 10.34 | 11.27 |
| 14/10/75 | 1.64 | 6.65 | 7.65 |
| 15/10/75 | - | NO DUST DISCARDED | - |
| 16/10/75 | 2.40 | 7.35 | 9.16 |
| 17/10/75 | 1.88 | 6.00 | 7.32 |
| 18/10/75 | 1.86 | 6.02 | 7.22 |
| 19/10/75 | 1.77 | 6.12 | 7.13 |
| 20/10/75 | - | NO SAMPLE | - |
| 21/10/75 | - | NO DUST DISCARDED | - |
| 22/10/75 | 2.08 | 6.23 | 7.83 |
| 23/10/75 | 1.41 | 5.65 | 6.70 |
| 24/10/75 | 3.08 | 6.05 | 8.60 |
| 25/10/75 | 5.11 | 5.56 | 10.07 |
| 26/10/75 | 4.28 | 5.49 | 9.28 |
| 27/10/75 | 4.01 | 5.22 | 8.63 |
| 28/10/75 | 4.39 | 5.15 | 8.87 |
| 29/10/75 | 3.89 | 4.84 | 8.21 |
| 30/10/75 | - | NO SAMPLE | - |
| 31/10/75 | - | NO SAMPLE | - |
| 1/11/75 | 6.79 | 3.62 | 9.62 |
| 2/11/75 | 6.62 | 3.27 | 9.38 |
| 3/11/75 | 5.85 | 3.10 | 8.57 |
| 4/11/75 | 5.82 | 2.81 | 8.34 |
| 5/11/75 | 3.09 | 4.08 | 7.46 |
| 6/11/75 | 1.35 | 4.12 | 5.83 |
| 7/11/75 | 1.07 | 4.11 | 5.47 |
| 8/11/75 | 0.75 | 3.76 | 4.67 |
| 9/11/75 | 0.83 | 4.13 | 5.42 |
| 2/12/75 | 5.33 | 5.84 | 9.36 |
| 3/12/75 | 4.14 | 6.37 | 8.78 |
| 4/12/75 | 2.64 | 6.51 | 7.81 |
| 5/12/75 | 7.14 | 12.66 | 16.28 |
| 6/12/75 | 4.76 | 6.28 | 9.10 |
| 7/12/75 | 5.75 | 6.41 | 9.88 |
| 8/12/75 | 6.24 | 6.97 | 10.70 |
| 9/12/75 | 4.76 | 5.41 | 8.24 |

TABLE C.3 (CONT'D)

| Date | % Cl | % $SO_3$ (Total S as) | % $K_2O$ |
|---|---|---|---|
| 10/12/75 | 5.35 | 5.51 | 8.27 |
| 11/12/75 | 5.52 | 4.90 | 8.20 |
| 12/12/75 | 5.53 | 5.62 | 8.46 |
| 13/12/75 | - | NO SAMPLE | - |
| 14/12/75 | 5.68 | 5.54 | 8.65 |
| 31/12/75 | - | NO SAMPLE | - |
| 1/ 1/76 | 1.98 | 6.19 | 6.88 |
| 2/ 1/76 | - | NO SAMPLE | - |
| 3/ 1/76 | - | NO SAMPLE | - |
| 4/ 1/76 | 4.55 | 4.62 | 7.37 |
| 5/ 1/76 | 4.58 | 4.62 | 7.38 |
| 6/ 1/76 | 4.03 | 4.70 | 6.89 |
| 7/ 1/76 | - | NO SAMPLE | - |
| 8/ 1/76 | 3.06 | 5.31 | 7.25 |
| 9/ 1/76 | 4.50 | 4.51 | 7.60 |
| 10/ 1/76 | 1.20 | 5.43 | 6.07 |
| 11/ 1/76 | 1.11 | 5.27 | 5.79 |
| 12/ 1/76 | 1.01 | 5.16 | 5.54 |
| 13/ 1/76 | 1.20 | 5.37 | 6.10 |
| 14/ 1/76 | 0.76 | 4.94 | 5.16 |
| 15/ 1/76 | 0.92 | 4.89 | 5.15 |
| 16/ 1/76 | 0.80 | 4.41 | 4.62 |
| 17/ 1/76 | 0.78 | 4.50 | 4.68 |
| 18/ 1/76 | 0.69 | 4.28 | 4.49 |
| 19/ 1/76 | 0.72 | 5.01 | 5.32 |
| 20/ 1/76 | 0.76 | 4.81 | 5.19 |
| 21/ 1/76 | 0.86 | 4.28 | 4.84 |

## TABLE C.4. RESULTS FROM ANALYSES OF RETURN DUST

| Date | % Cl | % $SO_3$ (Total S as) | % $K_2O$ |
|---|---|---|---|
| 7/10/75 | 0.80 | 6.25 | 6.22 |
| 8/10/75 | 0.73 | 6.28 | 6.25 |
| 9/10/75 | 0.54 | 5.36 | 5.15 |
| 10/10/75 | 0.73 | 7.26 | 7.54 |
| 11/10/75 | 1.59 | 7.05 | 8.20 |
| 12/10/75 | 1.36 | 7.79 | 8.90 |
| 13/10/75 | 1.29 | 6.21 | 7.02 |
| 14/10/75 | 2.46 | 8.16 | 9.83 |
| 15/10/75 | 2.29 | 6.91 | 8.54 |
| 16/10/75 | 2.15 | 6.80 | 8.32 |
| 17/10/75 | 2.33 | 7.20 | 8.73 |
| 18/10/75 | 1.81 | 5.61 | 6.71 |
| 19/10/75 | 1.86 | 6.51 | 7.73 |
| 20/10/75 | 1.76 | 5.86 | 7.08 |
| 21/10/75 | 2.56 | 6.54 | 8.44 |
| 22/10/75 | 1.53 | 6.00 | 6.92 |
| 23/10/75 | 1.52 | 5.37 | 6.60 |
| 24/10/75 | 3.82 | 5.36 | 8.63 |
| 25/10/75 | 3.41 | 4.87 | 7.75 |
| 26/10/75 | 3.87 | 4.84 | 8.21 |
| 27/10/75 | 3.48 | 4.48 | 7.47 |
| 28/10/75 | 3.02 | 4.75 | 6.91 |
| 29/10/75 | 3.51 | 4.24 | 7.23 |
| 30/10/75 | - | NO SAMPLE | - |
| 31/10/75 | 4.22 | 2.58 | 6.49 |
| 1/11/75 | 4.66 | 2.84 | 7.07 |
| 2/11/75 | 6.37 | 3.22 | 9.05 |
| 3/11/75 | 3.96 | 2.47 | 6.28 |
| 4/11/75 | 4.00 | 2.70 | 6.69 |
| 5/11/75 | 1.27 | 3.60 | 5.20 |
| 6/11/75 | 1.00 | 3.67 | 4.91 |
| 7/11/75 | 0.79 | 3.77 | 4.92 |
| 8/11/75 | 0.54 | 3.54 | 4.50 |
| 9/11/75 | 0.44 | 3.30 | 3.89 |
| 10/11/75 | - | NO SAMPLE | - |
| 2/12/75 | 4.00 | 5.65 | 10.70 |
| 3/12/75 | 2.52 | 5.97 | 9.63 |
| 4/12/75 | 2.49 | 6.51 | 8.58 |
| 5/12/75 | 2.58 | 6.96 | 8.33 |
| 6/12/75 | 1.00 | 3.69 | 4.94 |
| 7/12/75 | 0.79 | 3.81 | 4.93 |
| 8/12/75 | 0.58 | 3.57 | 4.61 |
| 9/12/75 | 3.68 | 4.68 | 6.59 |

TABLE C.4 (CONT'D)

| Date | % Cl | % $SO_3$ (Total S as) | % $K_2O$ |
|---|---|---|---|
| 10/12/75 | 2.51 | 3.68 | 4.60 |
| 11/12/75 | 2.36 | 3.45 | 4.22 |
| 12/12/75 | 3.69 | 4.22 | 5.94 |
| 13/12/75 | 4.04 | 4.07 | 6.05 |
| 14/12/75 | 3.02 | 4.06 | 5.16 |
| 31/12/75 | 1.56 | 5.09 | 5.60 |
| 1/ 1/76 | 1.78 | 5.14 | 5.99 |
| 2/ 1/76 | 1.77 | 4.70 | 5.65 |
| 3/ 1/76 | 2.42 | 4.62 | 5.82 |
| 4/ 1/76 | 3.55 | 4.48 | 6.33 |
| 5/ 1/76 | 2.37 | 3.36 | 4.29 |
| 6/ 1/76 | 2.56 | 3.43 | 4.64 |
| 7/ 1/76 | 1.35 | 3.23 | 3.58 |
| 8/ 1/76 | 1.76 | 4.91 | 5.56 |
| 9/ 1/76 | 2.30 | 3.71 | 4.91 |
| 10/ 1/76 | 1.06 | 4.74 | 5.05 |
| 11/ 1/76 | 0.93 | 5.05 | 5.46 |
| 12/ 1/76 | 0.80 | 5.14 | 5.37 |
| 13/ 1/76 | 0.79 | 4.82 | 5.10 |
| 14/ 1/76 | 0.78 | 4.85 | 4.93 |
| 15/ 1/76 | 0.78 | 4.41 | 4.59 |
| 16/ 1/76 | 0.65 | 4.27 | 4.38 |
| 17/ 1/76 | 0.58 | 4.11 | 4.10 |
| 18/ 1/76 | 0.69 | 4.19 | 4.22 |
| 19/ 1/76 | 0.58 | 4.56 | 4.70 |
| 20/ 1/76 | 0.72 | 4.47 | 4.62 |
| 21/ 1/76 | 0.87 | 4.24 | 4.83 |

TABLE C.5. Btu AND CHLORINE CONTENT OF CHLORINATED HYDROCARBONS (SAMPLES FROM LIME TO KILN)

| Material | Date | Btu/lb | % Chlorine | Viscosity (Centipoise @ 23°C) | Specific Gravity |
|---|---|---|---|---|---|
| Aliphatic | 24/10/75 | 13400 | 21.52 | | |
| | 27/10/75 | 11390 | 32.76 | | |
| | 28/10/75 | 10750 | 39.40 | | |
| | 3/11/75 | 8900 | 42.23 | | |
| | 4/11/75 | 8590 | 43.52 | | |
| | 13/11/75 | 8340 | 42.38 | | |
| | 18/11/75 | 8410 | 43.38 | | |
| | Average | 9970 | 37.88 | - | 1.13 |
| Aromatic + Complex | 10/12/75 | 9530 | 40.56 | | |
| | 11/12/75 | 9500 | 45.91 | | |
| | 12/12/75 | 8820 | 44.16 | | |
| | 13/13/75 | 9320 | 41.80 | | |
| | 15/12/75 | 9310 | 40.48 | | |
| | Average | 9300 | 42.58 | 40.8 | 1.27 |
| Polychlorinated Biphenyl | 3/ 1/76 | 11380 | 36.16 | | |
| | 4/ 1/76 | 11590 | 37.75 | | |
| | 5/ 1/76 | 11880 | 34.90 | | |
| | 6/ 1/76 | 12170 | 33.90 | | |
| | 7/ 1/76 | 12070 | 33.19 | | |
| | 8/ 1/76 | 12050 | 34.93 | | |
| | 9/ 1/76 | 12000 | 33.90 | | |
| | Average | 11880 | 34.97 | 17.0 | 1.18 |

TABLE C.6. Btu, S AND Cl ANALYSES FROM NO. 6 FUEL OIL

| Date | Btu/lb | % S | % Cl |
|---|---|---|---|
| 7/10/75 | 17809 | 2.40 | |
| 8/10/75 | 17222 | 2.42 | |
| 9/10/75 | 17978 | 2.34 | |
| 10/10/75 | 17942 | 2.26 | Average<br>7/10/75 - 22/10/75<br>% Chlorine = 0.028% |
| 14/10/75 | 18106 | 2.26 | |
| 15/10/75 | 18008 | 2.28 | |
| 16/10/75 | 17920 | 2.31 | |
| 17/10/75 | 17988 | 2.30 | |
| 20/10/75 | 17924 | 2.24 | |
| 21/10/75 | 17877 | 2.24 | |
| 22/10/75 | 17984 | 2.09 | |
| 23/10/75 | 18189 | 2.23 | |
| 24/10/75 | 17701 | 2.22 | |
| 27/10/75 | 17901 | 2.24 | |
| 28/10/75 | 17862 | 2.22 | |
| 29/10/75 | 17970 | 1.95 | |
| 30/10/75 | 17917 | 2.29 | |
| 31/10/75 | 17889 | 1.77 | |
| 3/11/75 | 18135 | 1.62 | |
| 4/11/75 | 18077 | 1.57 | |
| 5/11/75 | 18047 | 1.55 | |
| 6/11/75 | 18079 | 1.51 | Average<br>23/10/75-12/11/75<br>% Chlorine = 0.064 |
| 7/11/75 | 18036 | 1.56 | |
| 10/11/75 | 17979 | 1.26 | |
| 11/11/75 | 17782 | 1.89 | |
| 12/11/75 | 17719 | 2.06 | |
| 2/12/75 | 17700 | 2.54 | |
| 3/12/75 | 17676 | 2.28 | |
| 4/12/75 | 17714 | 2.56 | |
| 5/12/75 | 17648 | 2.58 | |
| 8/12/75 | 17679 | 2.55 | Average<br>2/12/75-15/12/75<br>% Chlorine = 0.047 |
| 9/12/75 | 17732 | 2.52 | |
| 10/12/75 | 17695 | 2.58 | |
| 11/12/75 | 17596 | 2.50 | |
| 12/12/75 | 17655 | 2.56 | |
| 15/12/75 | 17504 | 2.64 | |
| 30/12/75 | 17678 | 2.59 | |
| 2/ 1/76 | 17565 | 2.41 | |
| 5/ 1/76 | 17498 | 1.61 | Average<br>30/12/75-9/1/76<br>% Chlorine = 0.030 |
| 6/ 1/76 | 17433 | 2.07 | |
| 7/ 1/76 | 17630 | 2.28 | |
| 8/ 1/76 | 17900 | 2.47 | |
| 9/ 1/76 | 17719 | 2.42 | |
| 12/ 1/76 | 17990 | 1.96 | |
| 13/ 1/76 | 17896 | 1.95 | |

TABLE C.6 (CONT'D)

| Date | Btu/lb | % S | % Cl |
|---|---|---|---|
| 14/ 1/76 | 17935 | 1.54 | |
| 15/ 1/76 | 17952 | 2.00 | |
| 16/ 1/76 | 18025 | 1.98 | Average<br>12/1/76-22/1/76<br>% Chlorine = 0.038 |
| 19/ 1/76 | 17762 | 1.92 | |
| 20/ 1/76 | 17846 | 1.89 | |
| 21/ 1/76 | 18005 | 1.54 | |
| 22/ 1/76 | 18160 | 1.42 | |

TABLE C.7. DAILY RECORD OF PRODUCTION AND MATERIALS CONSUMPTION

| Date | SLURRY FEED (tons/24 hr) | CHLORIN. HC (gal/24 hr) | CLINKER (tons/24 hr) | DISCARD DUST (tons/24 hr) |
|---|---|---|---|---|
| 7/10/75 | 1653 | 0 | 1043 | 40.44 |
| 8/10/75 | 1676 | 0 | 1041 | 63.44 |
| 9/10/75 | 1681 | 0 | 1073 | 24.84 |
| 10/10/75 | 1658 | 0 | 1027 | 65.66 |
| 11/10/75 | 1585 | 0 | 1029 | 0 |
| 12/10/75 | 1325 | 0 | 845 | 18.94 |
| 13/10/75 | 1632 | 0 | 1036 | 6.96 |
| 14/10/75 | 1604 | 0 | 1047 | 23.00 |
| 15/10/75 | 1639 | 0 | 1064 | 0 |
| 16/10/75 | 1646 | 0 | 1058 | 12.90 |
| 17/10/75 | 1661 | 0 | 1065 | 17.86 |
| 18/10/75 | 1682 | 0 | 1081 | 15.32 |
| 19/10/75 | 1669 | 0 | 1079 | 4.93 |
| 20/10/75 | 1669 | 0 | 1071 | 15.97 |
| 21/10/75 | 1661 | 0 | 1078 | 0 |
| 22/10/75 | 1664 | 0 | 1046 | 45.36 |
| 23/10/75 | 1681 | 1170 | 1082 | 11.96 |
| 24/10/75 | 1686 | 1440 | 1079 | 19.72 |
| 25/10/75 | 1669 | 1440 | 1067 | 20.96 |
| 26/10/75 | 1732 | 1440 | 1112 | 16.42 |
| 27/10/75 | 1656 | 1440 | 1061 | 18.32 |
| 28/10/75 | 1652 | 1440 | 1040 | 42.58 |
| 29/10/75 | 1621 | 1440 | 1021 | 41.36 |
| 30/10/75 | 1633 | 2670 | 1032 | 37.17 |
| 31/10/75 | 1647 | 2880 | 1027 | 56.52 |
| 1/11/75 | 1658 | 2880 | 1029 | 63.32 |
| 2/11/75 | 1673 | 2880 | 1057 | 38.92 |
| 3/11/75 | 1679 | 2880 | 1030 | 80.66 |
| 4/11/75 | 1679 | 930 | 1010 | 107.72 |
| 5/11/75 | 1692 | 0 | 1044 | 72.82 |
| 6/11/75 | 1693 | 0 | 1054 | 60.46 |
| 7/11/75 | 1698 | 0 | 1058 | 59.90 |
| 8/11/75 | 1670 | 0 | 1030 | 73.50 |
| 9/11/75 | 1701 | 0 | 1056 | 64.26 |
| 2/12/75 | 1622 | 430 | 1038 | 20.58 |
| 3/12/75 | 1627 | 0 | 1042 | 18.30 |
| 4/12/75 | 1644 | 0 | 1039 | 37.72 |
| 5/12/75 | 1653 | 1640 | 1028 | 61.40 |
| 6/12/75 | 1670 | 2187 | 1056 | 38.26 |
| 7/12/75 | 1655 | 1351 | 1074 | 0 |
| 8/12/75 | 1666 | 1117 | 1043 | 51.36 |
| 9/12/75 | 1664 | 2121 | 984 | 129.78 |

TABLE C.7. (CONT'D)

| Date | SLURRY FEED (tons/24 hr) | CHLORIN. HC (gal/24 hr) | CLINKER (tons/24 hr) | DISCARD DUST (tons/24 hr) |
|---|---|---|---|---|
| 10/12/75 | 1676 | 1997 | 994 | 127.66 |
| 11/12/75 | 1669 | 1308 | 999 | 113.76 |
| 12/12/75 | 1669 | 1821 | 1024 | 79.12 |
| 13/12/75 | 1661 | 1691 | 985 | 125.96 |
| 14/12/75 | 1653 | 1869 | 956 | 157.68 |
| 15/12/75 | 1658 | 1909 | 980 | 130.30 |
| 31/12/75 | 1606 | 0 | 1024 | 24.72 |
| 1/ 1/76 | 1595 | 0 | 1035 | 0 |
| 2/ 1/76 | 1608 | 0 | 1039 | 6.11 |
| 3/ 1/76 | 1630 | 2029 | 1017 | 55.43 |
| 4/ 1/76 | 1629 | 2210 | 1005 | 70.90 |
| 5/ 1/76 | 1627 | 2168 | 970 | 116.98 |
| 6/ 1/76 | 1616 | 1985 | 1034 | 19.86 |
| 7/ 1/76 | 1612 | 604 | 944 | 137.39 |
| 8/ 1/76 | 1615 | 1230 | 1045 | 4.54 |
| 9/ 1/76 | 1619 | 1367 | 1027 | 32.10 |
| 10/ 1/76 | 1621 | 0 | 1020 | 43.92 |
| 11/ 1/76 | 1627 | 0 | 1011 | 61.20 |
| 12/ 1/76 | 1636 | 0 | 1032 | 40.52 |
| 13/ 1/76 | 1639 | 0 | 1040 | 32.36 |
| 14/ 1/76 | 1618 | 0 | 1028 | 42.80 |
| 15/ 1/76 | 1633 | 0 | 1046 | 19.10 |
| 16/ 1/76 | 1596 | 0 | 1026 | 13.38 |
| 17/ 1/76 | 1606 | 0 | 979 | 85.76 |
| 18/ 1/76 | 1635 | 0 | 1026 | 47.62 |
| 19/ 1/76 | 1608 | 0 | 1020 | 32.22 |
| 20/ 1/76 | 1602 | 0 | 991 | 66.56 |
| 21/ 1/76 | 1629 | 0 | 1016 | 55.75 |

TABLE C.8. MATERIAL BALANCE FOR CHLORINE

| DATE | CHLORINE INPUT (lb/24 hr) |  |  |  | CHLORINE RETAINED (lb/24 hr) |  |  | TOTAL % RETAINED |
|---|---|---|---|---|---|---|---|---|
|  | SLURRY FEED | #6 OIL | CHLORINATED HYDROCARBON | TOTAL | CLINKER | DISCARD DUST | TOTAL |  |
| 7/10/75 | 2,645 | 81 | 0 | 2,726 | 688 | 801 | 1,489 | 54.6 |
| 8/10/75 | 1,877 | 81 | 0 | 1,958 | 666 | 1,281 | 1,947 | 99.4 |
| 9/10/75 | 1,748 | 82 | 0 | 1,830 | 730 | 442 | 1,172 | 64.0 |
| 10/10/75 | 1,923 | 81 | 0 | 2,004 | 836 | 1,261 | 2,097 | 104.6 |
| 11/10/75 | 1,902 | 78 | 0 | 1,980 | 658 | 0 | 658 | 33.2 |
| 12/10/75 | 1,801 | 67 | 0 | 1,868 | 490 | 511 | 1,001 | 53.6 |
| 13/10/75 | 1,632 | 81 | 0 | 1,713 | 622 | 349 | 971 | 56.7 |
| 14/10/75 | 1,412 | 80 | 0 | 1,492 | 649 | 754 | 1,403 | 94.0 |
| 15/10/75 | 1,508 | 81 | 0 | 1,589 | 660 | 0 | 660 | 41.5 |
| 16/10/75 | 1,416 | 81 | 0 | 1,497 | 656 | 619 | 1,275 | 85.2 |
| 17/10/75 | 1,694 | 81 | 0 | 1,775 | 746 | 672 | 1,418 | 79.9 |
| 18/10/75 | 1,850 | 81 | 0 | 1,931 | 627 | 570 | 1,197 | 62.0 |
| 19/10/75 | 1,535 | 81 | 0 | 1,616 | 690 | 174 | 864 | 53.5 |
| 20/10/75 | 1,435 | 81 | 0 | 1,516 | 900 | 575 | 1,475 | 97.3 |
| 21/10/75 | 1,262 | 80 | 0 | 1,342 | 647 | 0 | 647 | 48.2 |
| 22/10/75 | 1,331 | 81 | 0 | 1,412 | 607 | 1,887 | 2,494 | 176.6 |
| 23/10/75 | 1,345 | 185 | 2,845 | 4,375 | 649 | 337 | 986 | 22.5 |
| 24/10/75 | 1,686 | 183 | 3,502 | 5,371 | 647 | 1,215 | 1,862 | 34.7 |
| 25/10/75 | 1,435 | 183 | 3,959 | 5,577 | 619 | 2,142 | 2,761 | 49.5 |
| 26/10/75 | 1,905 | 190 | 4,416 | 6,511 | 689 | 1,406 | 2,095 | 32.2 |
| 27/10/75 | 1,391 | 182 | 4,873 | 6,446 | 658 | 1,469 | 2,127 | 33.0 |
| 28/10/75 | 1,553 | 182 | 6,411 | 8,146 | 707 | 3,738 | 4,445 | 54.6 |
| 29/10/75 | 1,783 | 183 | 6,642 | 8,608 | 653 | 3,218 | 3,871 | 45.0 |
| 30/10/75 | 1,502* | 181 | 12,316 | 13,999 | 805 | 3,970* | 4,775 | 34.1 |
| 31/10/75 | 1,647 | 186 | 13,284 | 15,117 | 698 | 6,036* | 6,734 | 44.5 |
| 1/11/75 | 1,558 | 179 | 13,284 | 15,021 | 803 | 8,599 | 9,402 | 62.6 |
| 2/11/75 | 1,439 | 179 | 13,284 | 14,902 | 676 | 5,153 | 5,829 | 39.1 |
| 3/11/75 | 1,444 | 178 | 13,284 | 14,906 | 659 | 9,437 | 10,096 | 67.7 |
| 4/11/75 | 1,478 | 179 | 13,743 | 15,400 | 566 | 12,539 | 13,105 | 85.1 |
| 5/11/75 | 1,421 | 184 | 4,574 | 6,179 | 647 | 4,500 | 5,147 | 83.3 |
| 6/11/75 | 1,422 | 182 | 0 | 1,604 | 653 | 1,632 | 2,285 | 142.4 |

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* Calculated from average data.

TABLE C.8 (CONT'D)

| DATE | CHLORINE INPUT (lb/24 hr) SLURRY FEED | #6 OIL | CHLORINATED HYDROCARBON | TOTAL | CHLORINE RETAINED (lb/24 hr) CLINKER | DISCARD DUST | TOTAL | TOTAL % RETAINED |
|---|---|---|---|---|---|---|---|---|
| 7/11/75 | 1,494 | 183 | 0 | 1,677 | 783 | 1,282 | 2,065 | 123.1 |
| 8/11/75 | 1,403 | 181 | 0 | 1,584 | 597 | 1,102 | 1,699 | 107.3 |
| 9/11/75 | 1,701 | 182 | 0 | 1,883 | 739 | 1,067 | 1,806 | 95.9 |
| 2/12/75 | 1,492 | 124 | 2,325 | 3,941 | 644 | 2,194 | 2,838 | 72.0 |
| 3/12/75 | 1,367 | 133 | 0 | 1,500 | 604 | 1,515 | 2,119 | 141.3 |
| 4/12/75 | 1,348 | 133 | 0 | 1,481 | 708 | 1,992 | 2,700 | 182.3 |
| 5/12/75 | 1,322 | 132 | 8,868 | 10,322 | 678 | 8,768 | 9,446 | 91.5 |
| 6/12/75 | 1,336 | 131 | 11,826 | 13,293 | 612 | 3,642 | 4,254 | 32.0 |
| 7/12/75 | 1,721 | 131 | 7,306 | 9,158 | 601 | 0 | 601 | 6.6 |
| 8/12/75 | 1,366 | 142 | 6,040 | 7,548 | 793 | 6,410 | 7,203 | 95.4 |
| 9/12/75 | 1,331 | 132 | 11,470 | 12,933 | 787 | 12,355 | 13,142 | 101.6 |
| 10/12/75 | 1,374 | 130 | 10,287 | 11,791 | 676 | 13,660 | 14,336 | 121.6 |
| 11/12/75 | 1,302 | 134 | 7,626 | 9,062 | 699 | 12,559 | 13,258 | 146.3 |
| 12/12/75 | 1,669 | 134 | 10,213 | 12,016 | 655 | 8,751 | 9,406 | 78.3 |
| 13/12/75 | 1,395 | 133 | 8,977 | 10,505 | 630 | 14,208 | 14,838 | 141.2 |
| 14/12/75 | 1,587 | 131 | 10,107 | 11,825 | 593 | 17,906 | 18,499 | 156.4 |
| 31/12/75 | 1,895 | 85 | 0 | 1,980 | 594 | 979 | 1,573 | 79.4 |
| 1/ 1/76 | 1,340 | 87 | 0 | 1,427 | 600 | 0 | 600 | 42.0 |
| 2/ 1/76 | 1,447 | 87 | 0 | 1,534 | 603 | 242 | 845 | 55.1 |
| 3/ 1/76 | 1,402 | 83 | 8,657 | 10,142 | 671 | 4,434 | 5,105 | 50.3 |
| 4/ 1/76 | 1,499 | 82 | 9,844 | 11,425 | 603 | 6,452 | 7,055 | 61.8 |
| 5/ 1/76 | 1,236 | 83 | 8,928 | 10,247 | 679 | 10,715 | 11,394 | 111.2 |
| 6/ 1/76 | 1,228 | 83 | 7,950 | 9,261 | 641 | 1,601 | 2,242 | 24.2 |
| 7/ 1/76 | 1,548 | 85 | 2,366 | 3,999 | 548 | 10,991 | 11,539 | 288.5 |
| 8/ 1/76 | 1,260 | 83 | 5,070 | 6,413 | 627 | 278 | 905 | 14.1 |
| 9/ 1/76 | 1,554 | 81 | 5,468 | 7,103 | 575 | 2,889 | 3,464 | 48.8 |
| 10/ 1/76 | 1,556 | 109 | 0 | 1,665 | 571 | 1,054 | 1,625 | 97.6 |
| 11/ 1/76 | 1,562 | 109 | 0 | 1,671 | 607 | 1,359 | 1,966 | 117.6 |
| 12/ 1/76 | 1,309 | 109 | 0 | 1,418 | 619 | 818 | 1,437 | 101.3 |
| 13/ 1/76 | 1,344 | 108 | 0 | 1,452 | 603 | 777 | 1,380 | 95.0 |

TABLE C.8 (CONT'D)

| DATE | CHLORINE INPUT (lb/24 hr) |  |  |  | CHLORINE RETAINED (lb/24 hr) |  |  | TOTAL % RETAINED |
|---|---|---|---|---|---|---|---|---|
|  | SLURRY FEED | #6 OIL | CHLORINATED HYDROCARBON | TOTAL | CLINKER | DISCARD DUST | TOTAL |  |
| 14/ 1/76 | 1,424 | 108 | 0 | 1,532 | 617 | 650 | 1,267 | 82.7 |
| 15/ 1/76 | 1,372 | 108 | 0 | 1,480 | 607 | 351 | 958 | 64.7 |
| 16/ 1/76 | 1,532 | 107 | 0 | 1,639 | 616 | 214 | 830 | 50.6 |
| 17/ 1/76 | 1,317 | 108 | 0 | 1,425 | 724 | 1,338 | 2,062 | 144.7 |
| 18/ 1/76 | 1,776 | 108 | 0 | 1,874 | 575 | 657 | 1,232 | 65.7 |
| 19/ 1/76 | 1,254 | 107 | 0 | 1,361 | 571 | 464 | 1,035 | 76.0 |
| 20/ 1/76 | 1,282 | 107 | 0 | 1,389 | 575 | 1,012 | 1,587 | 114.2 |
| 21/ 1/76 | 1,336 | 109 | 0 | 1,445 | 589 | 959 | 1,548 | 107.1 |

TABLE C.9. MATERIAL BALANCE FOR $K_2O$

| | $K_2O$ INPUT (tons/24 hr) | $K_2O$ RETAINED (tons/24 hr) | | | TOTAL % RETAINED |
|---|---|---|---|---|---|
| DATE | SLURRY FEED | CLINKER | DUST | TOTAL | |
| 7/10/75 | 15.21 | 11.78 | 2.98 | 14.76 | 97.0 |
| 8/10/75 | 15.25 | 11.66 | 4.73 | 16.39 | 107.5 |
| 9/10/75 | 15.30 | 12.23 | 1.82 | 14.05 | 91.8 |
| 10/10/75 | 15.09 | 9.04 | 5.03 | 14.07 | 93.2 |
| 11/10/75 | 14.58 | 13.07 | 0 | 13.07 | 89.6 |
| 12/10/75 | 12.18 | 9.13 | 1.56 | 0.69 | 87.8 |
| 13/10/75 | 15.18 | 11.29 | 0.78 | 2.07 | 79.5 |
| 14/10/75 | 14.76 | 12.04 | 1.76 | 13.80 | 93.5 |
| 15/10/75 | 15.24 | 15.64 | 0 | 15.64 | 102.6 |
| 16/10/75 | 15.31 | 12.27 | 1.18 | 13.45 | 87.8 |
| 17/10/75 | 15.45 | 13.95 | 1.31 | 15.26 | 98.8 |
| 18/10/75 | 15.64 | 13.40 | 1.11 | 14.51 | 92.8 |
| 19/10/75 | 15.52 | 13.06 | 0.35 | 13.41 | 86.4 |
| 20/10/75 | 15.52 | 13.71 | 1.27* | 14.98 | 96.5 |
| 21/10/75 | 15.28 | 16.28 | 0 | 16.28 | 106.5 |
| 22/10/75 | 15.48 | 13.39 | 3.55 | 16.94 | 109.4 |
| 23/10/75 | 15.63 | 11.47 | 0.80 | 12.27 | 78.5 |
| 24/10/75 | 15.68 | 12.95 | 1.70 | 14.65 | 93.4 |
| 25/10/75 | 15.35 | 8.86 | 2.11 | 10.97 | 71.5 |
| 26/10/75 | 16.11 | 3.79 | 1.52 | 15.31 | 95.0 |
| 27/10/75 | 15.07 | 10.61 | 1.58 | 12.19 | 30.9 |
| 28/10/75 | 15.20 | 13.62 | 3.78 | 17.40 | 114.5 |
| 29/10/75 | 15.08 | 13.99 | 3.40 | 17.39 | 115.3 |
| 30/10/75 | 15.02* | 9.91 | 2.91* | 12.82 | 85.4 |
| 31/10/75 | 14.99 | 5.03 | 4.42* | 9.45 | 63.0 |
| 1/11/75 | 15.09 | 3.70 | 6.09 | 9.79 | 64.9 |
| 2/11/75 | 15.39 | 4.44* | 3.65 | 8.09 | 52.6 |
| 3/11/75 | 15.61 | 4.94 | 6.91 | 11.85 | 75.9 |
| 4/11/75 | 15.45 | 5.66 | 8.88 | 14.54 | 94.1 |
| 5/11/75 | 15.74 | 10.44 | 5.43 | 15.87 | 100.8 |
| 6/11/75 | 15.58 | 12.44 | 3.52 | 15.96 | 102.4 |
| 7/11/75 | 15.62 | 12.70 | 3.28 | 15.98 | 102.3 |
| 8/11/75 | 15.20 | 11.84 | 3.43 | 15.27 | 100.5 |
| 9/11/75 | 15.99 | 12.57 | 3.48 | 16.05 | 100.4 |
| 2/12/75 | 14.60 | 9.76 | 1.93 | 11.69 | 80.1 |
| 3/12/75 | 14.64 | 13.34 | 1.61 | 14.95 | 102.1 |
| 4/12/75 | 14.63 | 10.49 | 2.94 | 13.43 | 91.8 |
| 5/12/75 | 15.04 | 11.92 | 10.00 | 21.92 | 145.7 |
| 6/12/75 | 15.03 | 9.50 | 3.48 | 12.98 | 86.4 |
| 7/12/75 | 15.06 | 9.02 | 0 | 9.02 | 59.9 |
| 8/12/75 | 15.16 | 7.72 | 5.50 | 3.22 | 87.2 |
| 9/12/75 | 14.81 | 5.51 | 0.69 | 16.20 | 109.4 |
| 10/12/75 | 15.25 | 3.58 | 10.56 | 14.14 | 92.7 |
| 11/12/75 | 15.19 | 4.80 | 9.33 | 14.13 | 93.0 |

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* Calculated from average data.

TABLE C.9 (CONT'D)

| | $K_2O$ INPUT (tons/24 hr) | $K_2O$ RETAINED (tons/24 hr) | | | TOTAL % RETAINED |
|---|---|---|---|---|---|
| DATE | SLURRY FEED | CLINKER | DUST | TOTAL | |
| 12/12/75 | 15.19 | 5.53 | 6.69 | 12.22 | 80.4 |
| 13/12/75 | 14.95 | 3.94 | 10.71* | 14.55 | 97.3 |
| 14/12/75 | 15.04 | 4.59 | 13.64 | 18.23 | 121.2 |
| 31/12/75 | 14.45 | 12.29 | 1.70* | 13.99 | 96.8 |
| 1/ 1/76 | 14.51 | 13.87 | 0 | 13.87 | 95.6 |
| 2/ 1/76 | 14.79 | 14.23 | 0.42* | 14.65 | 99.0 |
| 3/ 1/76 | 14.83 | 7.83 | 4.01 | 11.84 | 79.8 |
| 4/ 1/76 | 14.99 | 14.27 | 5.22 | 19.49 | 130.0 |
| 5/ 1/76 | 14.80 | 7.57 | 8.63 | 16.20 | 109.4 |
| 6/ 1/76 | 14.70 | 6.00 | 1.37 | 7.37 | 50.1 |
| 7/ 1/76 | 14.67 | 11.89 | 0.93* | 21.82 | 148.7 |
| 8/ 1/76 | 14.37 | 8.67 | 0.33 | 9.00 | 62.6 |
| 9/ 1/76 | 14.89 | 4.72 | 2.44 | 7.16 | 48.1 |
| 10/ 1/76 | 14.75 | 10.71 | 2.66 | 13.37 | 90.6 |
| 11/ 1/76 | 14.80 | 11.32 | 3.54 | 14.87 | 100.4 |
| 12/ 1/76 | 14.89 | 11.87 | 2.24 | 14.11 | 94.8 |
| 13/ 1/76 | 15.08 | 14.04 | 1.97 | 16.01 | 106.2 |
| 14/ 1/76 | 14.72 | 13.16 | 2.21 | 15.37 | 104.4 |
| 15/ 1/76 | 14.86 | 12.76 | 0.98 | 13.74 | 92.5 |
| 16/ 1/76 | 14.52 | 14.88 | 0.62 | 15.50 | 106.7 |
| 17/ 1/76 | 14.45 | 13.90 | 4.01 | 17.91 | 123.9 |
| 18/ 1/76 | 14.88 | 13.03 | 2.14 | 15.17 | 101.9 |
| 19/ 1/76 | 14.63 | 11.73 | 1.71 | 13.44 | 91.9 |
| 20/ 1/76 | 14.58 | 14.47 | 3.45 | 17.92 | 122.9 |
| 21/ 1/76 | 14.99 | 11.38 | 2.70 | 14.08 | 93.9 |

* Calculated from average data.

## APPENDIX D

## QUALITY OF CEMENT PRODUCED

While remote, the possibility of non-volatile chlorinated hydrocarbons not being destroyed and remaining with the clinker was considered. It is common knowledge that excessive quantities of organic materials can detrimentally affect setting, air entraining and compressive strength characteristics of cement.

After preparing the daily composite clinker sample for analysis, the quantity of sample which had not undergone size reduction was retained. These were combined into a composite of several days, three such composites being prepared for each of the aromatic plus complex chlorinated hydrocarbon burn, the PCB burn and the final baseline burn. Each composite, after being crushed to approximately one-half inch, was blended with the correct amount of the normal production gypsum used at St. Lawrence Cement. The clinker-gypsum blends were ground in a laboratory ball mill. The grinding was timed and samples were taken at suitable intervals during grinding to determine surface area.

The cements were produced to conform to the requirements of Symbol 10 cement as designated in the Canadian Standards Association (CSA) Standard A5 "Portland Cements", and Type I cement as defined in the American Society for Testing and Materials (ASTM) designation C150, "Standard Specification for Portland Cement".

Each cement was tested in conformance to the following ASTM methods:

C185, Test for Air Content of Hydraulic Cement Mortar;
C109, Test for Compressive Strength of Hydraulic Cement Mortars (using 2-in. cube specimens);
C359, Test for False Set of Portland Cement (Mortar Method);
C204, Test for Fineness of Portland Cement by Air Permeability Apparatus;
C151, Test for Autoclave Expansion of Portland Cement;
C191, Test for Time of Setting of Hydraulic Cement by Vicat Needle.

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To ensure that differences in quality were not due to unexpected differences in cement composition, a chemical analysis was performed on each cement tested. Procedures followed were those normally used for control purposes at St. Lawrence Cement.

The technique used for determination of the concentration of each oxide was fusion with lithium tetraborate followed by x-ray fluorescence analysis. This method is commonly used for cement analyses. With the exception of lower $K_2O$ content in the cements from clinkers produced while burning chlorinated hydrocarbons, there were no significant differences in their chemical compositions (Tables D.1, D.2 and D.3).

Differences in physical characteristics found by testing these cements were:

Setting Time - The water required to obtain normal consistency was greater and setting time shorter for baseline clinker cements. Shorter time of set and higher water requirement were attributed to the higher alkali content of the baseline clinker.

False Set - False set was severe on the cements from clinker produced during baseline burning. There was no indication of false set in cements from clinker produced while burning chlorinated hydrocarbons. The improvement was due to lower alkali content of the cement. In this regard, the determination of false set by ASTM Method C451, "Test for False Set of Portland Cement (Paste Method)" would not have shown as dramatic an improvement. This latter test takes into account the water requirement of cements, and therefore compensates for the greater quantity of water required by the higher alkali cements.

Compressive Strength - Higher initial and lower ultimate strengths are characteristics of higher alkali content cements. The only apparent differences in cements from clinkers produced with and without burning of chlorinated hydrocarbons were those expected because of the differences in alkali content.

TABLE D.1. CEMENTS FROM CLINKER PRODUCED DURING BASELINE BURN

| Sample Number | 7 | 8 | 9 | Aver. |
|---|---|---|---|---|
| **Chemical Tests** | | | | |
| Loss on Ignition (%) | 1.52 | 1.51 | 1.43 | 1.49 |
| $SiO_2$ (%) | 20.69 | 20.59 | 20.53 | 20.60 |
| $Al_2O_3$ " | 5.93 | 5.90 | 6.00 | 5.94 |
| $Fe_2O_3$ " | 2.20 | 2.22 | 2.24 | 2.22 |
| CaO " | 63.42 | 63.39 | 63.35 | 63.39 |
| MgO " | 2.52 | 2.52 | 2.52 | 2.52 |
| $SO_3$ " | 2.74 | 2.79 | 2.89 | 2.81 |
| $K_2O$ " | 1.15 | 1.23 | 1.22 | 1.20 |
| Free CaO (%) | 0.44 | 0.52 | 0.54 | 0.50 |
| $C_3S$ (%) | 50.1 | 50.8 | 50.0 | 50.3 |
| $C_2S$ " | 21.6 | 20.8 | 21.2 | 21.2 |
| $C_3A$ " | 12.0 | 11.9 | 12.1 | 12.0 |
| $C_4AF$ " | 6.7 | 6.7 | 6.8 | 6.7 |
| **Physical Tests** | | | | |
| Fineness | | | | |
| Blaine ($cm^2$/g) | 3406 | 3579 | 3607 | 3530 |
| Passing 200 mesh (%) | 96.4 | 97.6 | 98.8 | 97.6 |
| Setting Time | | | | |
| N.C. Penetration (mm) | 10.0 | 9.5 | 9.0 | 9.5 |
| N.C. Water (%) | 22.5 | 23.0 | 23.0 | 22.8 |
| Initial (minutes) | 115 | 106 | 106 | 109 |
| Final (minutes) | 225 | 216 | 221 | 221 |
| False Set | | | | |
| Temperature °F | 70 | 73 | 73 | 72 |
| Penetration (mm) | | | | |
| 3 minutes | 50 | 37 | 34 | 40 |
| 5 minutes | 50 | 7 | 8 | 22 |
| 8 minutes | 21 | 4 | 4 | 10 |
| 11 minutes | 16 | 4 | 3 | 8 |
| Remix | 50 | 50 | 50 | 50 |
| Compressive Strength | | | | |
| 1 day (psi) | 2050 | 2010 | 1910 | 1990 |
| 3 day (psi) | 2910 | 2990 | 3210 | 3040 |
| 7 day (psi) | 3480 | 3610 | 3880 | 3660 |
| 28 day (psi) | 4130 | 4470 | 4530 | 4380 |
| Air Content | | | | |
| Water (%) | 73.0 | 73.0 | 73.0 | 73.0 |
| Flow (%) | 80.6 | 86.8 | 86.0 | 84.5 |
| Air (%) | 7.2 | 7.6 | 8.3 | 7.7 |
| Autoclave Expansion (%) | 0.07 | 0.09 | 0.05 | 0.07 |

TABLE D.2. CEMENTS FROM CLINKER PRODUCED DURING AROMATIC PLUS COMPLEX CHLORINATED HYDROCARBON BURN

| Sample Number | 4 | 5 | 6 | Aver. |
|---|---|---|---|---|
| **Chemical Tests** | | | | |
| Loss on Ignition (%) | 1.63 | 1.86 | 1.63 | 1.71 |
| $SiO_2$ (%) | 20.37 | 20.51 | 20.83 | 20.57 |
| $Al_2O_3$ (%) | 5.85 | 5.79 | 5.89 | 5.84 |
| $Fe_2O_3$ (%) | 2.26 | 2.23 | 2.22 | 2.24 |
| CaO (%) | 63.19 | 62.99 | 63.56 | 63.25 |
| MgO (%) | 2.51 | 2.49 | 2.52 | 2.51 |
| $SO_3$ (%) | 2.81 | 2.69 | 2.89 | 2.80 |
| $K_2O$ (%) | 0.66 | 0.53 | 0.69 | 0.63 |
| Free CaO (%) | 0.50 | 0.59 | 0.48 | 0.52 |
| $C_3S$ (%) | 51.8 | 50.8 | 49.4 | 50.7 |
| $C_2S$ (%) | 19.4 | 20.6 | 22.5 | 20.8 |
| $C_3A$ (%) | 11.7 | 11.6 | 11.9 | 11.7 |
| $C_4AF$ (%) | 6.9 | 6.8 | 6.7 | 6.8 |
| **Physical Tests** | | | | |
| Fineness | | | | |
| Blaine ($cm^2/g$) | 3626 | 3562 | 3561 | 3583 |
| Passing 200 mesh (%) | 98.0 | 97.4 | 97.2 | 97.5 |
| Setting Time | | | | |
| N.C. Penetration (mm) | 10.0 | 10.0 | 9.5 | 9.8 |
| N.C. Water (%) | 22.0 | 22.0 | 22.0 | 22.0 |
| Initial (minutes) | 118 | 135 | 135 | 129 |
| Final (minutes) | 238 | 250 | 250 | 246 |
| False Set | | | | |
| Temperature °F | 70 | 72 | 73 | 72 |
| Penetration (mm) | | | | |
| 3 minutes | 50 | 50 | 50 | 50 |
| 5 minutes | 50 | 50 | 50 | 50 |
| 8 minutes | 50 | 50 | 50 | 50 |
| 11 minutes | 50 | 50 | 50 | 50 |
| Remix | 50 | 50 | 50 | 50 |
| Compressive Strength | | | | |
| 1 day (psi) | 1900 | 1640 | 1890 | 1810 |
| 3 day (psi) | 3520 | 3200 | 3180 | 3300 |
| 7 day (psi) | 4590 | 4360 | 4160 | 4370 |
| 28 day (psi) | 5900 | 6050 | 5460 | 5800 |
| Air Content | | | | |
| Water (%) | 71.0 | 72.0 | 72.0 | 71.6 |
| Flow (%) | 80.0 | 90.5 | 81.3 | 83.9 |
| Air (%) | 9.2 | 9.0 | 6.7 | 8.3 |
| Autoclave Expansion (%) | 0.03 | 0.04 | 0.02 | 0.03 |

TABLE D.3. CEMENTS FROM CLINKER PRODUCED DURING POLYCHLORINATED BIPHENYL BURN

| Sample Number | 1 | 2 | 3 | Aver. |
|---|---|---|---|---|
| Chemical Tests | | | | |
| Loss on Ignition (%) | 1.46 | 1.58 | 1.48 | 1.51 |
| $SiO_2$ (%) | 20.51 | 20.72 | 20.87 | 20.70 |
| $Al_2O_3$ (%) | 5.91 | 5.86 | 5.89 | 5.89 |
| $Fe_2O_3$ (%) | 2.16 | 2.18 | 2.16 | 2.17 |
| CaO (%) | 63.24 | 63.27 | 63.65 | 63.39 |
| MgO (%) | 2.53 | 2.56 | 2.58 | 2.56 |
| $SO_3$ (%) | 2.94 | 2.64 | 2.61 | 2.73 |
| $K_2O$ (%) | 1.01 | 0.74 | 0.96 | 0.90 |
| Free CaO (%) | 0.53 | 0.57 | 0.69 | 0.60 |
| $C_3S$ (%) | 50.4 | 50.0 | 50.3 | 50.2 |
| $C_2S$ (%) | 20.9 | 21.8 | 22.0 | 21.6 |
| $C_3A$ (%) | 12.0 | 11.9 | 12.0 | 12.0 |
| $C_4AF$ (%) | 6.6 | 6.6 | 6.6 | 6.6 |
| Physical Tests | | | | |
| Fineness | | | | |
| Blaine ($cm^2/g$) | 3388 | 3579 | 3593 | 3520 |
| Passing 200 mesh (%) | 96.0 | 97.0 | 96.8 | 96.6 |
| Setting Time | | | | |
| N.C. Penetration (mm) | 10.0 | 11.0 | 9.0 | 10.0 |
| N.C. Water (%) | 22.0 | 22.0 | 22.0 | 22.0 |
| Initial (minutes) | 153 | 125 | 112 | 130 |
| Final (minutes) | 273 | 250 | 235 | 253 |
| False Set | | | | |
| Temperature °F | 70 | 71 | 71 | 71 |
| Penetration (mm) | | | | |
| 3 minutes | 50 | 50 | 50 | 50 |
| 5 minutes | 50 | 50 | 50 | 50 |
| 8 minutes | 50 | 50 | 50 | 50 |
| 11 minutes | 50 | 50 | 50 | 50 |
| Remix | 50 | 50 | 50 | 50 |
| Compressive Strength | | | | |
| 1 day (psi) | 1980 | 1800 | 1990 | 1920 |
| 3 day (psi) | 3080 | 3000 | 3260 | 3110 |
| 7 day (psi) | 3770 | 4000 | 4090 | 3950 |
| 28 day (psi) | 4620 | 5110 | 5080 | 4940 |
| Air Content | | | | |
| Water (%) | 71.0 | 71.0 | 71.0 | 71.0 |
| Flow (%) | 88.0 | 84.5 | 82.2 | 84.9 |
| Air (%) | 7.7 | 7.9 | 9.2 | 8.3 |
| Autoclave Expansion (%) | 0.05 | 0.06 | 0.08 | 0.06 |

# APPENDIX E

## EQUIPMENT DESCRIPTION AND ASSOCIATED ECONOMICS

In order to burn waste chlorinated hydrocarbons in a cement kiln, they must be blended to be compatible with the handling and storage system and to achieve uniform feed to the kiln. A storage tank and feed system with associated control devices must be installed at the kiln site.

For the program to be economically viable, the price structure must be favourable to the originator of the wastes and to the cement producer. The waste disposal company must be able to generate sufficient revenue to cover shipping, handling, blending, disposal of non-fuel fractions and receive some profit. The economics from the point of view of the cement producer are discussed in Section E.2.

### E.1 Equipment Description

The system installed at the cement plant can vary. A simple inflexible installation with manual controls and a used rail car for storage would cost approximately $25,000. At the other extreme, a sophisticated system with large storage capacity, corrosion resistant construction, well instrumented could cost $200,000.

Although there are general similarities between cement kilns, the flow rate of waste chlorinated hydrocarbon depends on the percentage of chlorine in the waste, the decrease desired in the potassium and sodium levels of the finished product and the production capacity of the kiln. Thus, for the optimum system, the design, engineering, installation and operation must be compatible with these parameters.

Two systems are described herein; one is the actual system installed at the St. Lawrence Cement Co. kiln and the other has been somewhat arbitrarily selected as a basic system. This basic system assumes that a quality controlled blend of chemical wastes will be used. The fuel product would be a low viscosity, single-phase liquid, non-corrosive or mildly corrosive to carbon steel, not highly volatile, having an approximate composition of: 60,000 Btu/gallon, 40% Cl, and specific gravity of 1.2. Fuels with higher or lower Btu and chlorine can be prepared for those applications where other compositions are optimum.

Pages 134, 135, and 136 blank

At these compositional values, a feed rate of 1 lgpm into a 1000 ton per day kiln would provide an alkali reduction of 0.45% as $K_2O$. The Btu's provided would be a small percentage of the total heat requirement of the kiln. With waste streams with a lower chlorine level, larger volumes can be used to make up a greater fraction of the heat requirements, in practice up to 10-15% of total Btu input.

Other than capacity and the provision that the kiln be rotary, it makes little difference what the primary fuel or fuels are. Wet or dry fuels can burn waste chlorinated hydrocarbons, with consideration given to the increase in dust loading to the dust handling equipment.

### E.1.1 Cost of basic system

The basic system with minimum component cost estimates would entail:

| Equipment Cost: | |
|---|---|
| Tank, 10,000 gal carbon steel | $ 8,000 |
| Feed Pump, Centrifugal, 7.5 hp | 1,200 |
| Flame Arrestor | 100 |
| Vent Scrubber, Activated Carbon | 1,000 |
| Tank Level Indicator | 2,500 |
| Grounding | 400 |
| Tank Berming | 1,000 |
| Unloading Piping | 500 |
| Piping, Tank to Kiln, 100'- | 1,000 |
| Electrical-Combination Starter | 1,500 |
| Concrete Pad, Site Preparation | 2,500 |
| Miscellaneous, Hardware Painting and NFPA Code Marking | 2,500 |
| Instrumentation | 400 |
| Nozzle Assembly | 200 |
| | $22,800 |
| Installation: | 4,000 |
| Total System Cost, Installed | $26,800 |

A schematic representation of the system is shown in Figure E.1.

Operating Cost:

| | |
|---|---|
| Maintenance, 4% of investment/year | $1,080 |
| Operating Labour, Based on 330 days/year<br>Operating 24 hr/day<br>1 hr per shift @ $8.00 | 8,000 |
| Electricity, 7.5 hp, 8000 hr<br>@ 3¢/kwh | 1,800 |

Startup of the system should be achieved with minimum effort once the system is installed and tested for leaks. Allowance of $1,500 for initial startup should be adequate. Safety equipment for personnel protection and a fire exinguisher at the unloading/pumping station can be provided for about $250.

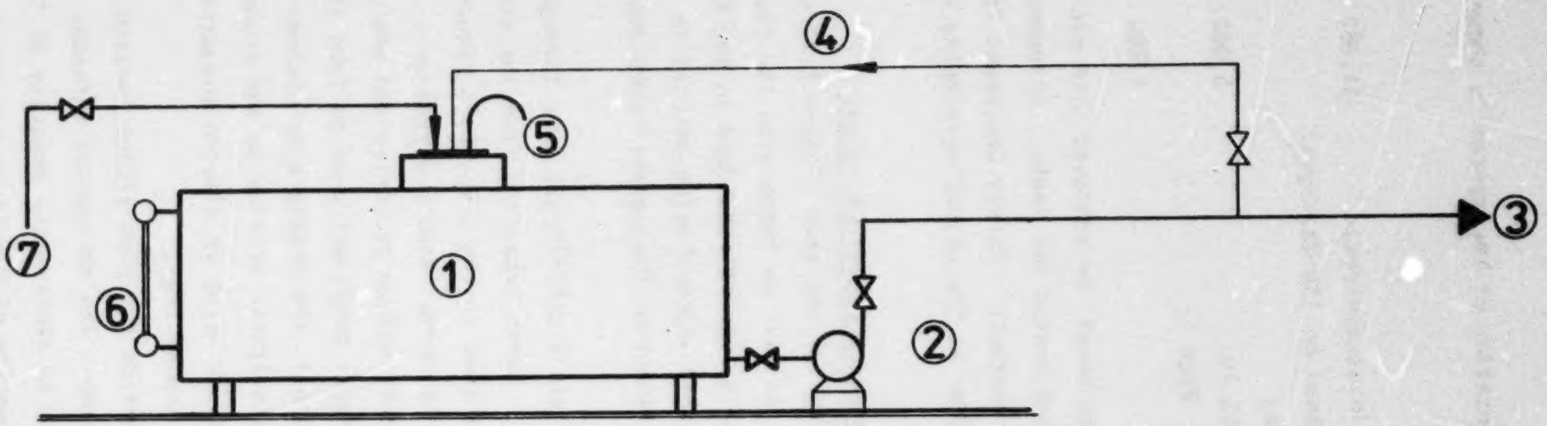
### E.2.2 System at the St. Lawrence Cement Co. plant

The actual system used for the test (Figure E.2) was designed to contain corrosive materials as well as those with low flash points. Sophisticated equipment is used to control the feed to the kiln and the system includes traps to avoid vapours being emitted to the atmosphere. The storage tank received two liners of "Furoglass" membrane and one liner of 2½" acid proof brick.

Trucks were unloaded via a centrifugal pump through filters into a 55,000 gal storage tank. Fumes exhausted from the storage tank while unloading trucks were returned to the truck by a return vent line. Fumes emanating from the tanks by normal vapour diffusion or expansion due to temperature were removed by sodium hydroxide and charcoal filters.

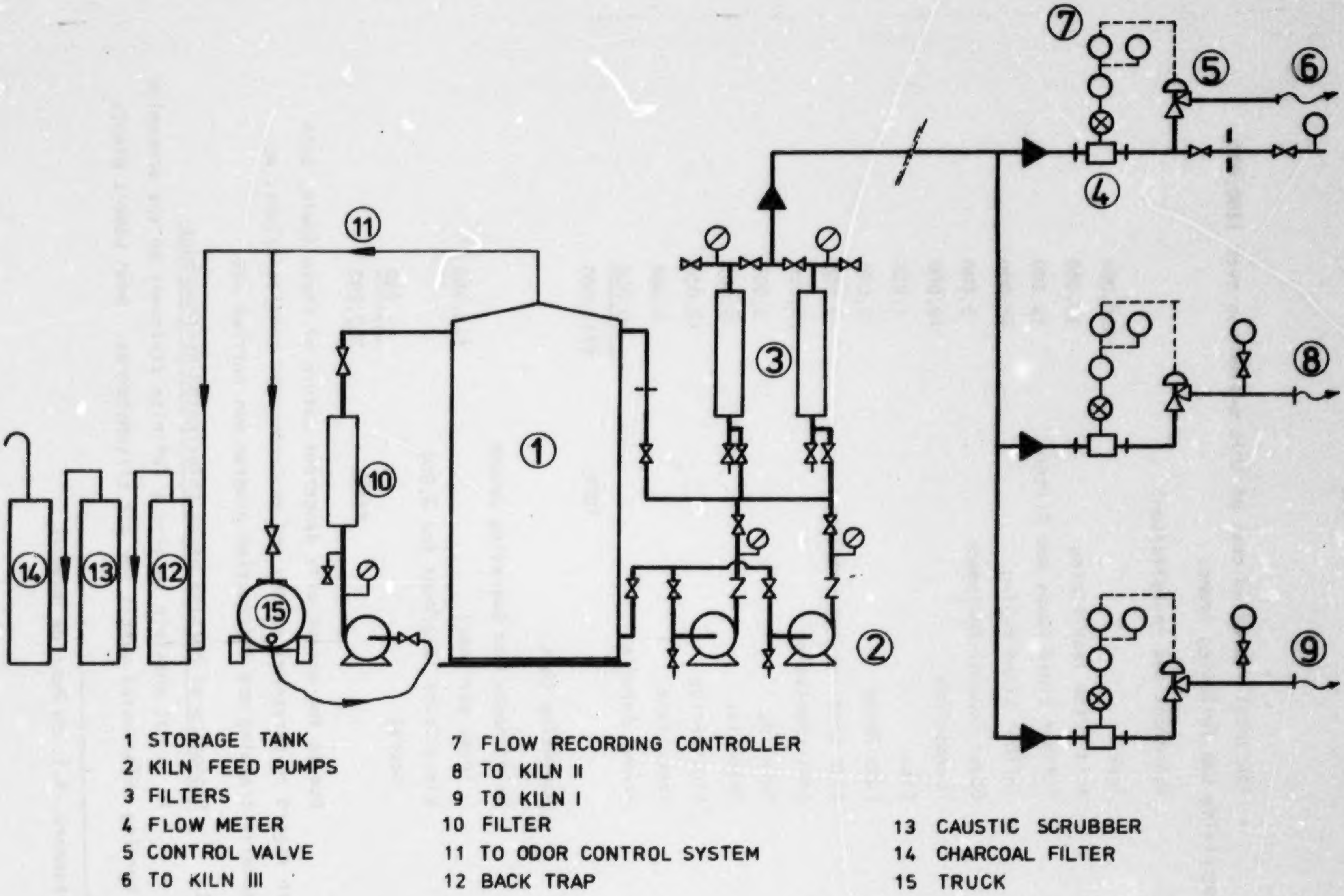
Either of two centrifugal pumps was used to feed the kilns at a pressure of approximately 120 psi, the pressure maintained by returning an amount of material through a suitable orifice to the storage tank. Each kiln was controlled separately using an electro-pneumatic control valve, magnetic flow meter and transmitter.

The tubing inserted inside the pipe sleeve located on top of the burners was made from tantalum. The tubing was threaded so that a titanium nozzle, of correct size to atomize the quantity of liquid input to the kiln, up to a maximum capacity of 4 gallons per minute, could be attached.



1 CHEMTROL STORAGE TANK
2 PUMP
3 TO KILN
4 RETURN LINE
5 VENT PIPE
6 LEVEL GAUGE
7 FILLER PIPE

FIGURE E.1 SCHEMATIC DIAGRAM OF BASIC CHLORINATED HYDROCARBON FEED SYSTEM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1 STORAGE TANK
2 KILN FEED PUMPS
3 FILTERS
4 FLOW METER
5 CONTROL VALVE
6 TO KILN III
7 FLOW RECORDING CONTROLLER
8 TO KILN II
9 TO KILN I
10 FILTER
11 TO ODOR CONTROL SYSTEM
12 BACK TRAP
13 CAUSTIC SCRUBBER
14 CHARCOAL FILTER
15 TRUCK

FIGURE E.2 SCHEMATIC DIAGRAM OF CHLORINATED HYDROCARBON FACILITIES

The total installed cost of this system was over $200,000, comprising the following items:

Equipment and Installation:

| | |
|---|---|
| Tank | $25,000 |
| Acid Brick Tank Lining | 35,000 |
| Teflon* Lined Pumps and Filters | 12,000 |
| Teflon* Lined Piping | 45,000 |
| Odour Control Equipment | 5,000 |
| Foundations | 10,000 |
| Dike | 1,000 |
| Pump House | 10,000 |
| Site Clearing and Leveling | 3,000 |
| Instrumentation | 20,000 |
| Painting | 5,000 |
| Sales Tax | 5,000 |
| Engineering | 18,000 |
| Consultant | 8,000 |
| Travel Expense | 10,000 |
| TOTAL | $212,000 |

Operating Cost:

| | |
|---|---|
| Maintenance and Operating Labour (cost per year) | $25,450 |
| Electricity (23¢/hour for 8,000 hours) | 1,840 |
| TOTAL | $27,290 |

Due to the potentially dangerous nature of these fuels, both with regard to personnel safety and environmental considerations, an extensive training and instruction program was carried out.

## E.2 Economics of Burning Waste Chlorinated Hydrocarbons

It is not possible to give a definite statement on the economics of burning chlorinated wastes for all circumstances. Some cement plants require a reduction in the alkali oxide ($K_2O + Na_2O$) content of the finished product. In this case, chlorine must be added to the process materials, and is available from different sources in different geographical areas. Waste hydrochloric acid from the steel industry may be used where available; in other areas cement plants purchase calcium chloride. If reduction of alkali is not required, then addition of chloride would cause the generation of greater quantities of dust, thereby increasing dust disposal costs.

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*Trademark, E.I. du Pont de Nemours.

Another factor making economic comparisons difficult is the different waste streams available. In some cases, the chlorinated waste streams may be suitable for purifying and further use. Other waste streams, such as PCB's and insecticides banned for environmental reasons, present a serious disposal problem. Obviously, these different materials would not all cost the same for use in a cement kiln. However, to present some models, the price structure used by Chemtrol Pollution Services, Inc. for blended noncorrosive wastes suitable for use in the basic system described above has been adopted. At present, Chemtrol plans to charge 80 percent of the fuel value and, where applicable, 30 percent of the chlorine value for these blended "fuels". In the examples, the following assumptions have been made: The kiln is a wet process type producing 1,000 tons per day with a fuel requirement equivalent to 5,150,000 Btu per ton of production.

### E.2.1 Process requiring addition of chlorine

Assume in this case that the fuel cost is $1 per million Btu and that it is necessary to reduce the $K_2O$ content of the clinker by 0.45 percent. This would require approximately 6,800 pounds of chlorine per day. A 32 percent solution of calcium chloride weighing 13 pounds and costing $0.14 per Imperial gallon ($0.053 per pound of chlorine) is used. In this case, 2,565 gallons would be required at a total cost of $359.

This could be replaced by "Trol Fuel*" containing a nominal 70 percent chlorine and 65,000 Btu per Imperial gallon. At a weight of 13 pounds per gallon, 750 gallons would be required each day. Using the above mentioned price structure, the cost per gallon would be:

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*Trademark, Chemtrol Pollution Services Inc.

$$9.1 \text{ lb } Cl_2 \times \frac{\$0.053}{\text{lb } Cl_2} \times \frac{30}{100} = \$0.145$$

$$65{,}000 \text{ Btu} \times \frac{\$1.00}{1{,}000{,}000 \text{ Btu}} \times \frac{80}{100} = \underline{\$0.052}$$

$$\text{TOTAL} \quad \$0.20$$

Thus, the 750 gallons would cost $150 and would supply 48.8 million Btu.

The total daily tangible savings then become:

| | |
|---|---|
| Cost of Calcium Chloride | $359 |
| Cost of Normal Fuel Replaced | $ 49 |
| Less Cost of "Trol Fuel" | $150 |
| Net Savings Per Day | $258 |

### E.2.2 Process not requiring addition of chlorine

The 1,000 ton per kiln and a specific heat consumption of 5,150,000 Btu per ton of clinker produced and a fuel cost equivalent to $1.00 per million Btu is again taken as the model. In this case, however, no chlorine is required and the waste stream contains less than 5 percent chlorine. This material is available at $0.80 per million Btu and is used at a replacement rate of 10 percent of the Btu requirement or 515,000 Btu per ton of clinker.

The fuel normally used on the kiln but replaced by this waste stream would cost $0.515 per ton of clinker or $515 per day. The daily savings can be calculated as:

| | |
|---|---|
| Cost of Normal Fuel Replaced | $515 |
| Cost of "Trol Fuel" | 412 |
| Net Daily Savings | $103 |

This saving can be negated by the cost of discarding the additional dust collected in the precipitators (See Section 6.1), a factor which will vary with each cement plant.

### E.2.3 Total economic considerations

The above models are not intended to be all inclusive. Due to the many variables involved, each possible application must be assessed based upon economic factors existing in the locale. At the time the system was installed at the St. Lawrence Cement Co., it was necessary to use chlorine in two wet kilns each having a capacity of 1,000 tons per year. For the period January through September 1976, maintenance on the system amounted to $18,760. Thus, the figure of $27,290 for yearly operating and maintenance cost is considered accurate. Under these circumstances, the economic picture over the period of a year becomes:

| | |
|---|---|
| Total Savings Using "Trol Fuel" (600 kiln operating days @ $258 per day) | $154,800 |
| Maintenance and Operating Cost | 27,290 |
| Interest on $212,000 @ 11%/year | 23,320 |
| Net | $104,190 |

This estimated saving, which would have given excellent payback on the system, has not been realized. Low alkali requirements have been falling into disfavour because such requirements are not compatible with the goal of energy conservation. With the requirement for chlorine addition, savings must be based only on fuel costs which, if all factors are favourable, would total for the two kilns:

| | |
|---|---|
| Total Savings Using "Trol Fuel" (600 kiln operating days @ $103/day) | $61,800 |
| Maintenance and Operating Costs | 27,290 |
| Interest on $212,000 @ 11%/yr | 23,320 |
| Net | $11,190 |

Even this modest sum has not been realized, for two reasons: the cost of discarding additional dust, and the unsteady supply of these wastes.

It is obvious from this discussion that plants requiring the addition of chlorine are in a better position to make burning of chlorinated wastes attractive than those plants not requiring chlorine. Also, a less sophisticated system than that installed at St. Lawrence Cement Co. is necessary if the only consideration is the fuel value of these wastes.

# APPENDIX F

## ONTARIO MINISTRY OF THE ENVIRONMENT EMISSION GUIDELINES AND ANALYTICAL SUPPORT

### F.1 Emission Guidelines

All industrial sources of potentially significant emissions to the atmosphere in Ontario come under the jurisdiction of the Province's Environmental Protection Act. The Act requires such sources to operate under a Certificate of Approval which specifies the acceptable operating conditions and emission rates for potential air contaminants. The Ministry of the Environment required that the experimental waste chlorinated hydrocarbon burn at St. Lawrence Cement Co., Mississauga meet certain conditions specified in a Certificate of Approval. Conditional approval was granted for each of the three stages of the waste burn (A, B, C) under the terms of the tentative guidelines for the allowable emission rates of organic chloride.

Pasquill-Gifford dispersion calculations based on the guideline emission rates from the wet kiln were used to predict the worst-case ground level concentration of residual organic chloride (½-hour average).

Table F.1 shows the specifications which were applied to each stage of the waste burn, along with the measured emission rates.

The less stringent guideline for the first two waste burns was met easily. Because of the large percentage of highly persistent polychlorinated biphenyls anticipated in the fuel for the third waste burn, a much more stringent guideline was given.

In the most critical case, the third burn, the calculated approximate flue gas concentration of residual chloride, 50 $\mu g/m^3$ (as Cl), based on the stated guideline, corresponds to roughly 5 ppb (v/v) of Aroclor 1242 or 17 ppb (v/v) of dichloromethane (at ambient temperature), the predominant individually identified component of the flue gas. These values compare with the detection limit for PCB's of 3 $\mu g/m^3$ or 0.3 ppb in the flue gas (ambient temperature).

Since no PCB was found in the flue gas samples and the methylene chloride concentration only slightly exceeded the very stringent guideline for organic chloride in this stage, the guideline should be considered to have been met without question.

Pages 146,147, and 148 blank

TABLE F.1. MOE SPECIFICATIONS APPLIED TO WASTE BURNS

| Waste Burn | 1 | 2 | 3 | 4 | 5* | 6 | 7 |
|---|---|---|---|---|---|---|---|
| A | 0.5 | 99.5 | 99.990 | 5000 | 23-150 | 0.2 | 0.001-0.006 |
| B | 0.5 | 99.5 | 99.989 | 5000 | 16-150 | 0.2 | 0.001-0.006 |
| C | 0.005 | 99.995 | 99.986 | 50 | 88-150 | 0.002 | 0.004-0.006 |

Column Identification:

1. Guideline emission rate for residual organic chloride (g Cl/sec).
2. Estimated required percent destruction or retention of chlorinated fuel.
3. Estimated minimum percent combustion of chlorinated fuel from test data (Table 6, Section 5.3).
4. Approximate calculated flue gas residual chloride concentration based on guideline emission rate (μg Cl/m$^3$).
5. Approximate measured flue gas organic chloride concentration based on dichloromethane and data from Table 5, Section 5.3 (μg Cl/m$^3$). The upper limit of the range corresponds to 50 ppb organic Cl as $CH_2Cl_2$.
6. Calculated point of impingement ½-hour average chloride concentration based on guideline emission rate (μg Cl/m$^3$).
7. Approximate calculated point of impingement ½-hour average chloride concentration based on dichloromethane and data from Tables 5 and 6, Section 5.3 (μg Cl/m$^3$).

---

*Since no PCB's were detected in the flue gas samples, none of the residual organic chloride values in column 5 should be attributed to PCB's in any of these stages.

If the concentration of residual organic chloride in the flue gas (column 7, Table F.1) were taken to represent PCB's in a "worst case" (recall that no PCB's were detected), the calculated point of impingement concentration by the Pasquill-Gifford method is approximately equal to typical measured ambient air concentrations of PCB's in urban areas. There would appear to be little cause for concern when the emission guidelines are met in this process configuration.

The above discussion relates only to the wet-kiln tests at St. Lawrence Cement. If the same guidelines were applied to another kiln, for example the lower-level, multi-stack dry kiln at St. Lawrence Cement, the same emission rate as measured in the wet kiln tests would lead to a significant ground level concentration. For example, even if the stringent guideline for PCB emissions were met in this hypothetical case, the maximum ground level concentration is calculated by virtual source methods (applied to the dry kiln stack configuration) to be 0.07 $\mu g/m^3$ (as Aroclor 1242) which is 7 to 70 times the typical measured ambient air concentration of 0.001 to 0.01 $\mu g/m^3$. The point is that some caution should be exercised in applying the results of these tests to another stack configuration.

In the case of the third waste burn, it was estimated that the total organic vapour concentration in the flue gas during the tests was about 50 ppb, of which about 30 ppb was found to be dichloromethane. Since none of the components of the original fuel mixture were detected, however, the maximum residual concentration of Aroclor 1242, for example, could be only about 1 ppb or less (noting the approximate detection limit of 0.3 ppb). For speculation purposes only, in this worst case, 1 ppb Aroclor 1242 in the flue gas (at ambient temperature) would correspond to about 11 $\mu g/m^3$ PCB (or about 5 $\mu g/m^3$ as chloride) and about 0.1 kg of Aroclor 1242 emitted per day (24 hours of continuous operation). In reality, this quantity is an overestimate of the total emissions and is probably not significant.

## F.2 Gas Chromatographic Analysis of Process and Emission Test Samples

### F.2.1 Chromosorb 102 adsorption tube analysis

Duplicate Chromosorb adsorption tubes for each of the waste burns were analyzed by the Air Quality Laboratory, Laboratory Services

Branch, Ontario Ministry of the Environment for support and cross-check of analytical results obtained by the Ontario Research Foundation. Each adsorption tube sample represented 60 litres of emission gas. Analysis was done after desorption at 120°C into an evacuated glass vessel by injecting a 1 ml gas sample into a gas chromatograph. This instrument was equipped with a 9 foot x 1/8 inch Chromosorb 102 column held at a temperature of 180°C, and a $Sc^3H$ electron capture detector.

The results from these analyses are summarized in Tables F.2 to F.4. All Chromosorb tube samples, including those from "Baseline B", were found to contain small but measurable amounts of six or seven compounds and traces of a further six to eight compounds. These "measurable" compounds were almost certainly chlorinated, low-molecular weight compounds which, in the tables, have been designated "major" and "minor", according to the size of their gas-chromatographic peaks. Of these compounds, only chloroform had been tentatively identified and quantitatively determined. All other compounds separated from each sample were estimated together by relating the sum of the gas chromatographic peak areas with those obtained from a chloroform standard. Their concentrations are listed under "Other Compounds".

The results shown in Tables F.2 to F.4 indicate that the total of all chlorinated compounds in the Chromosorb adsorption tube samples corresponds to concentrations only in the low parts per billion range in the stack emission gases.

The agreement between these results and those of the Ontario Research Foundation and TRW is only qualitative. The generally small amounts (ppb range) of organic chloride vapours found by ORF are confirmed but trends from stage to stage are not reproduced. Such disagreement is merely indicative that the limits of sensitivity of the combined sampling and analytical methods are being approached.

### F.2.2 Fuel feedstock analysis

Samples of the waste chlorinated hydrocarbon fuels used in waste burns B and C were analyzed in the laboratory of Professor F.W. Karasek, Department of Chemistry, University of Waterloo under a research grant from the Air Resources Branch, Ontario Ministry of the Environment.

TABLE F.2. ST. LAWRENCE CEMENT WASTE BURN EXPERIMENTS - TEST 1
CHROMOSORB ADSORPTION TUBE ANALYSIS

| Waste Burn Experiment | "Major" Compounds | "Minor" Compounds | Chloroform ppb | Other Compounds ppb | Total Compounds ppb |
|---|---|---|---|---|---|
| A | 3 | 4 | 1.192 | 7.121 | 8.313 |
| B | 1 | 5 | 0.058 | 0.646 | 0.704 |
| C | 2 | 4 | 0.329 | 2.909 | 3.238 |
| Baseline B | 2 | 5 | 0.055 | 2.487 | 2.542 |
| Blank (Chromosorb) | 0 | 0 | - | - | - |

TABLE F.3. ST. LAWRENCE CEMENT WASTE BURN EXPERIMENTS - TEST 2
CHROMOSORB ADSORPTION TUBE ANALYSIS

| Waste Burn Experiment | "Major" Compounds | "Minor" Compounds | Chloroform ppb | Other Compounds ppb | Total Compounds ppb |
|---|---|---|---|---|---|
| A | 4 | 3 | 1.462 | 8.827 | 10.289 |
| B | 4 | 1 | 1.464 | 5.270 | 6.734 |
| C | 3 | 4 | 0.924 | 12.089 | 13.013 |
| Baseline B | 0 | 7 | 0.022 | 0.443 | 0.465 |
| Blank (Chromosorb) | 0 | 0 | - | - | - |

TABLE F.4. ST. LAWRENCE CEMENT WASTE BURN EXPERIMENTS - TEST 3
CHROMOSORB ADSORPTION TUBE ANALYSIS

| Waste Burn Experiment | "Major" Compounds | "Minor" Compounds | Chloroform ppb | Other Compounds ppb | Total Compounds ppb |
|---|---|---|---|---|---|
| A | 5 | 0 | 2.356 | 15.773 | 18.129 |
| B | 3 | 3 | 0.481 | 1.916 | 2.397 |
| C | 3 | 8 | 0.560 | 2.089 | 2.649 |
| Baseline B | 3 | 4 | 0.030 | 5.077 | 5.107 |
| Blank (Chromosorb) | 0 | 0 | - | - | - |

F.2.2.1 Preparation of fuel samples. All samples were diluted ten times with Burdick and Jackson "Distilled in Glass" methylene chloride. A 0.1 ml aliquot of the fuel was made up to 1.0 ml with the methylene chloride.

Methylene chloride was chosen for the solvent based on previous fuel samples analyzed in this laboratory.

F.2.2.2 Analysis of fuel samples. All samples were surveyed by gas chromatography using a 10' x 2 mm i.d. glass column with a specially prepared, high resolution column packing, referred to as Ap-20M. A similarly prepared solution of Aroclor 1242 was also chromatographed for comparison.

The GC conditions used are shown in Table F.6 and were closely monitored by the use of a HP 5830 A Digital Gas Chromatograph using a flame ionization detector. The area of the solvent peak was rejected to facilitate comparison of GC data.

Mass spectral data were obtained using a Perkin-Elmer 900 GC interfaced to a HITACHI RMU-6 magnetic mass spectrometer via a Biemann - Watson effusion separator. The spectra were initiated and counted manually. All spectra were obtained with 70 eV ionizing voltage at 250°C.

Samples 1 and 9 were analyzed using GC/MS techniques as above.

### F.2.3 Results and Discussion

Samples 8 to 10, the aromatic chlorinated fuels, displayed only seven compounds with individual integrated area percentages greater than 1% and only nine with similar area percentages greater than 0.5%. There appear to be only three major components: one with *ca*. 73% area, one with *ca*. 4.5%, and one with *ca*. 6.8%. This appeared to be the case for all the aromatic fuels. A representative bar chromatogram is shown in Figure F.1. The peak at four minutes in the aromatic fuel was *ca*. 73%.

Samples 1 to 7, the PCB fuels, displayed several peaks in addition to those of the aromatic fuels, samples 8 to 12. Comparison of the additional peaks with a chromatogram of Aroclor 1242 indicates that these peaks are due almost entirely to PCB compounds (see Figure F.1).

To illustrate this observation, the GC data from the aromatic fuel was added to the GC data from Aroclor 1242 and the computer program

## TABLE F.5. FUEL SAMPLE IDENTIFICATION

| Sample No. | Comments |
|---|---|
| 1 | Chemtrol Line Sample (PCB's), Jan. 3/76, 10:00 AM |
| 2 | " " " " , Jan. 4/76, 12:00 |
| 3 | " " " " , Jan. 5/76 |
| 4 | " " " " , Jan. 6/76 |
| 5 | " " " " , Jan. 7/76, 9:00 AM |
| 6 | " " " " , Jan. 8/76, 8:45 |
| 7 | " " " " , Jan. 9/76* |
| 8 | Chemtrol Line Sample (Aromatics), Dec. 10/75** |
| 9 | " " " " , Dec. 11/75** |
| 10 | " " " " , Dec. 12/75** |
| 11 | " " " " , Dec. 13/75** |
| 12 | " " " " , Dec. 15/75** |

*Sample appeared to have water in it.

**Sample had reacted with liner of sample vial cap.

## TABLE F.6. GAS CHROMATOGRAPH CONDITIONS
## HP 5830-A GC

| | |
|---|---|
| TEMP 1 | $50^{\circ}$ |
| TIME | 4 min |
| RATE | $4^{\circ}$/min |
| TEMP 2 | $240^{\circ}$ |
| TIME 2 | 50 min |
| INJ TEMP | $280^{\circ}$ |
| FID TEMP | $300^{\circ}$ |
| FLOW RATE | 28 ml/min |
| CARRIER GAS | HELIUM |
| ATTENUATION | $2^8$ 256 |

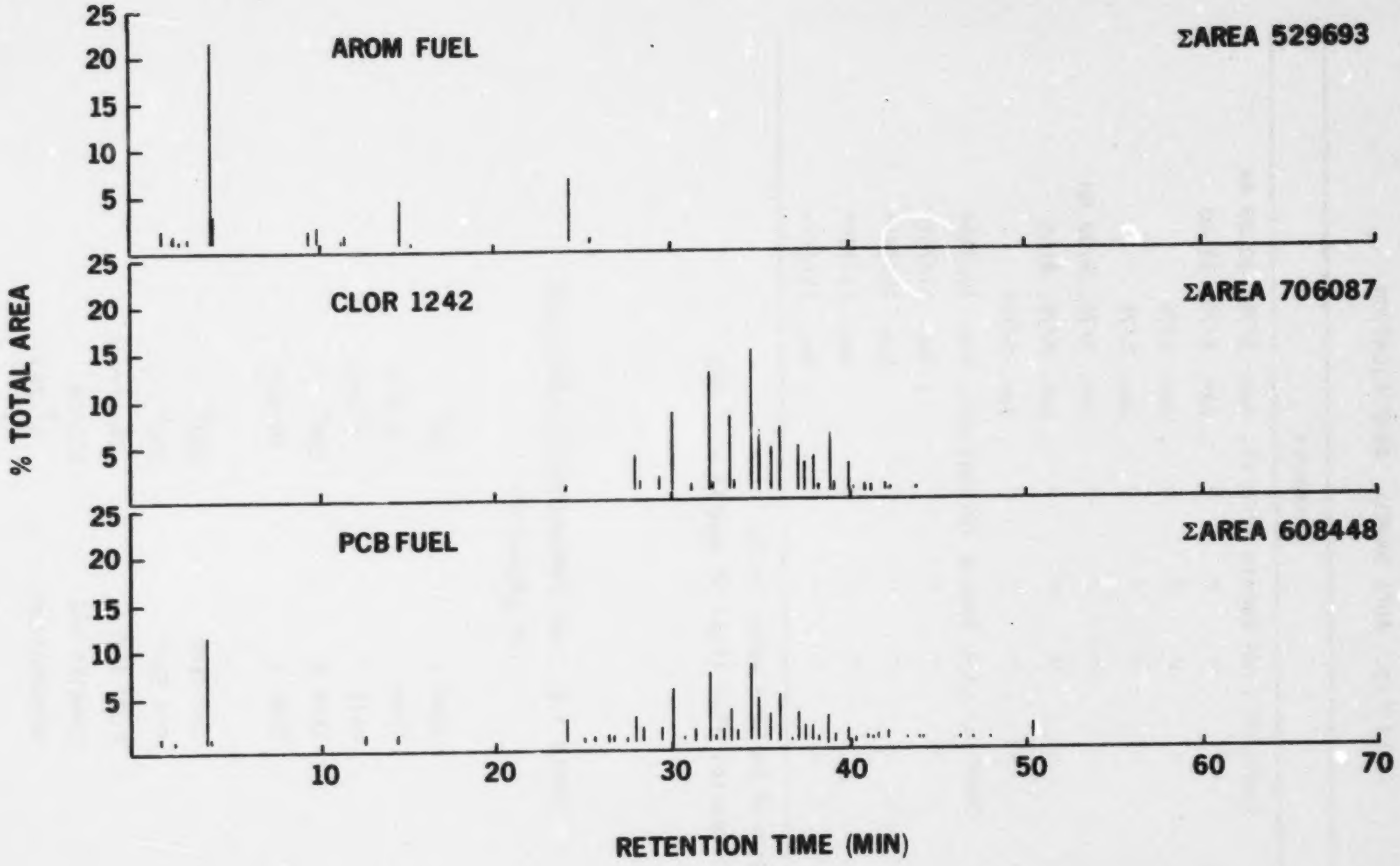

FIGURE F1 REPRESENTATIVE BAR CHROMATOGRAM

treated the data as though it originated from a single sample. This computer-produced bar chromatogram, titled "AROM + CLOR", was then plotted in comparison with the bar chromatogram of the PCB fuel sample as shown in Figure F.2. The data were not subjected to any manipulation other than straight combination of the data. Inspection of the two plots shows such a close correspondence of GC peaks between the computer reconstructed mixture and the actual PCB fuel mixture that there is a reasonable assurance they are the same.

A GC/MS analysis was conducted on sample 1, one of the PCB fuels. A representative gas chromatogram with numerically identified peaks is shown in Figure F.3. Mass spectra were obtained for these numerically identified peaks. The probable identity, molecular weight and/or degree of chlorination is shown in Table F.7.

Since all of the peaks are found in the PCB fuel and only some of the peaks are found in the aromatic fuel, an estimate of the dilution or mixing of these compounds can be derived. During the gas chromatograph analysis, all variables were held constant; thus, absolute integrated area counts are indicative of changes in relative concentrations. These results are shown in Table F.8. The units are area counts and the values shown are $1/10^4$ of output values.

Peak #3 is absent in the aromatic fuel and in Aroclor 1242 but present in the PCB fuel. The mass spectrum of peak #3 suggests trichlorobenzene.

Peak #19 is present in small amounts in the chlorinated aromatic fuels, absent in Aroclor 1242 but present in increased concentrations in the PCB fuels. A definitive mass spectrum of this peak was not obtained but was suggestive of lack of halogenation and is most likely an unsaturated hydrocarbon of high molecular weight.

### F.2.4 Conclusions

The aromatic fuel is primarily o-chlorotoluene and the PCB fuel is a mixture of Aroclor 1242 and the aromatic fuel. Area data for peak #1 indicated an initial dilution of approximately one-third (by comparison of area counts for aromatic fuels to area counts for sample 1) which increased to approximately four-fifths by the end of sampling data.

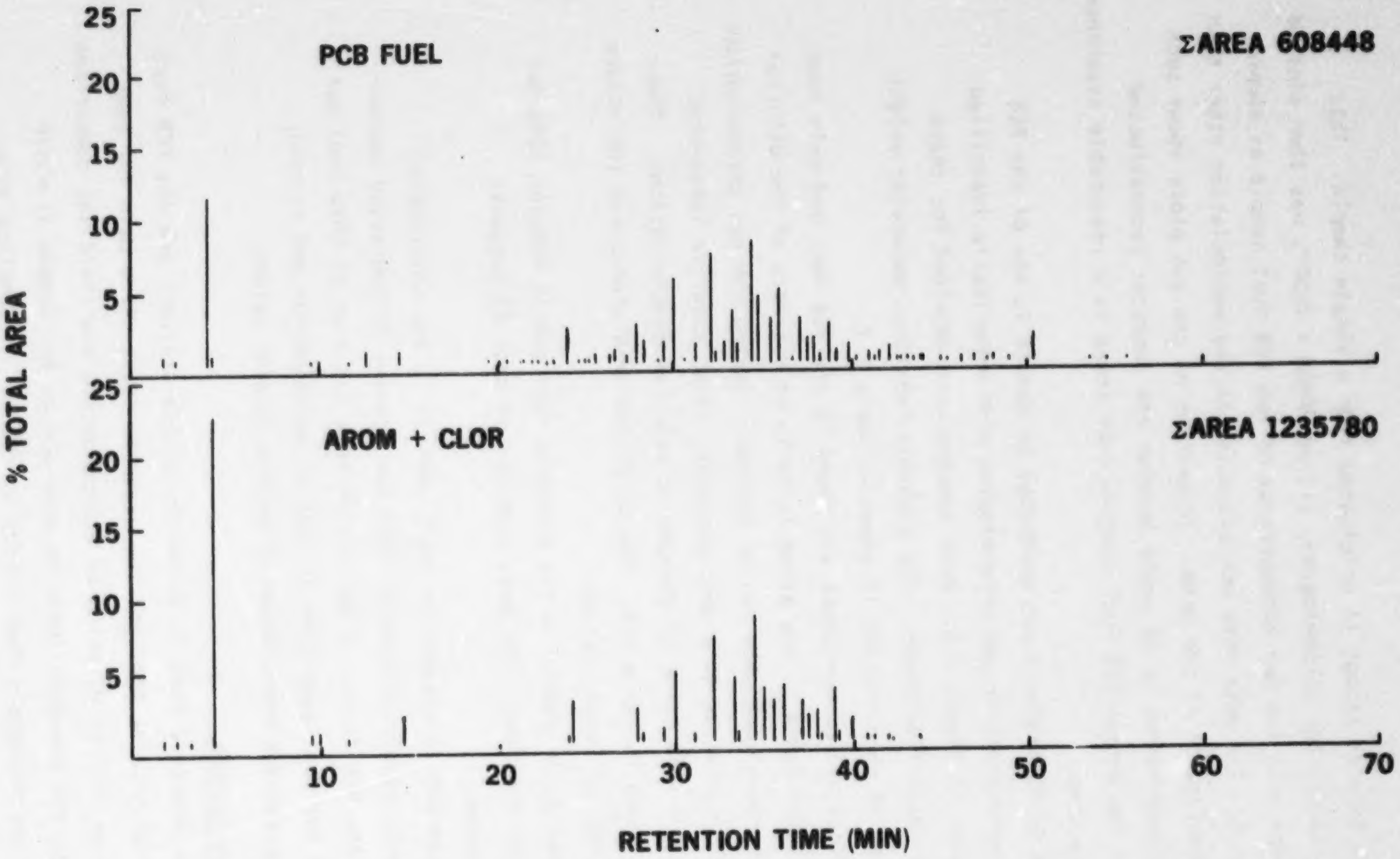

FIGURE F2 COMPUTER RECONSTRUCTED BAR CHROMATOGRAMS FOR PCB FUEL AND AROMATIC FUEL PLUS AROCHLOR 1242

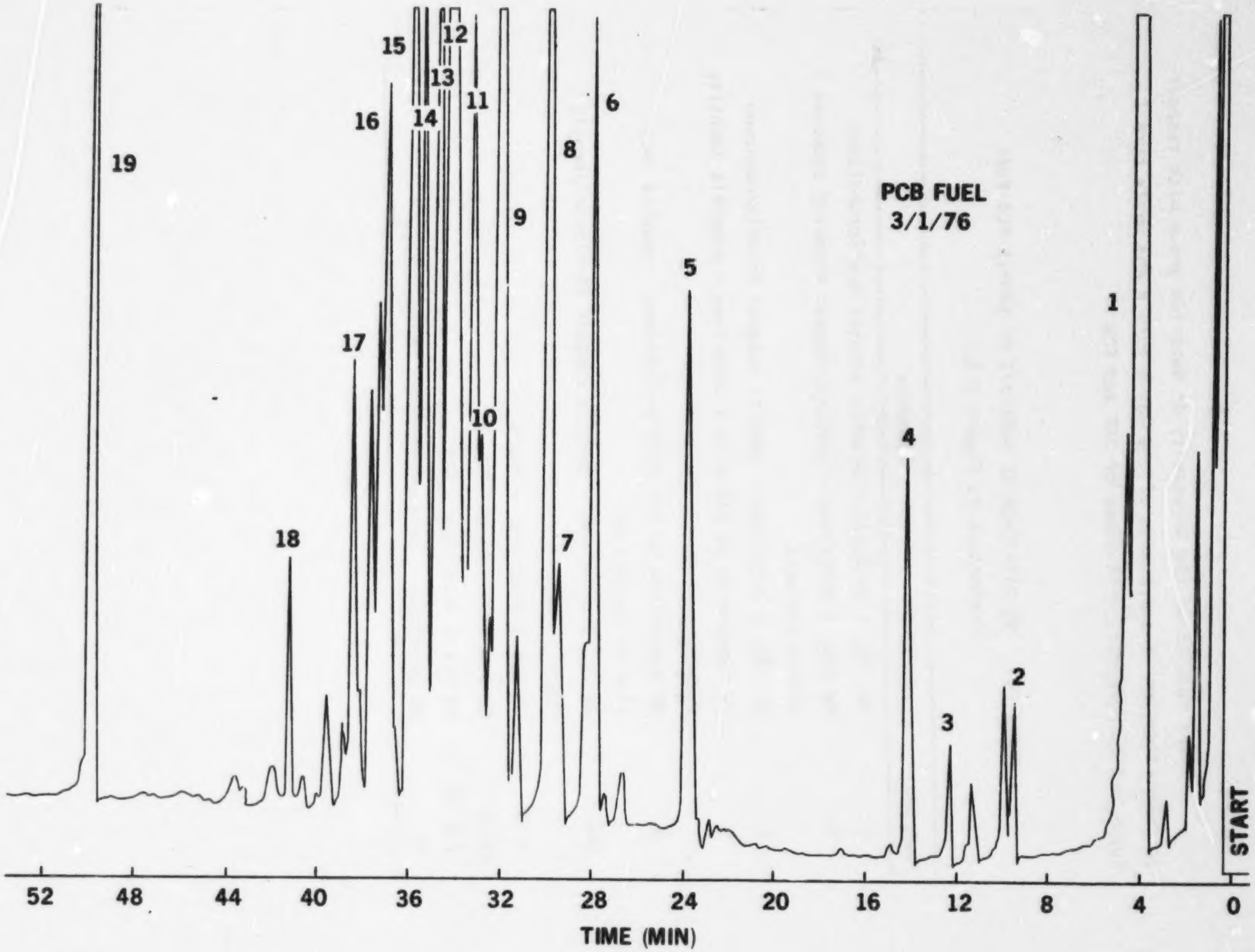

FIGURE F3 GAS CHROMATOGRAM FROM GC/MS ANALYSIS OF SAMPLE PCB FUEL

The results of the University of Waterloo group with respect to identification of components of the waste burn B and waste burn C fuels are in agreement with those of ORF and TRW.

TABLE F.7. MS DATA FROM GC ANALYSIS OF SAMPLE PCB FUEL
(Reference to Figure F.3.)

| Peak No. | Comments |
|---|---|
| 1 | MW 126, 1 chlorine - spectra suggest o-chlorotoluene |
| 2 | MW 160, 2 chlorines - spectra suggest aromatic compound - dichlorotoluene |
| 3 | MW 180, 3 chlorines - spectra suggest trichlorobenzene |
| 4 | MW appears to be 216 with 4 chlorines - possible identity $C_6H_4Cl_4$ |
| 5 | MW appears to be 216 with 4 chlorines - spectra very similar to peak #4 |
| 6-8 | MW 222 2 chlorines - spectra suggest dichlorobiphenyls - PCB's |
| 9-12 | MW 256 3 chlorines - PCB's |
| 13-16 | MW 290 4 chlorines - PCB's |
| 17 & 18 | MW 324 5 chlorines - PCB's |
| 19 | MW uncertain - no suggestion of halogenation |

TABLE F.8. AREA COUNTS (x 10k)

| Peak No. | 8<br>10/12/75 | 9<br>11/12/75 | 10<br>12/12/75 | 11<br>13/12/75 | 12<br>15/12/75 | 1<br>3/1/76 | 2<br>4/1/76 | 3<br>5/1/76 | 4<br>6/1/76 | 5<br>7/1/76 | 6<br>8/1/76 | 7<br>9/1/76 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 3860 | 3976 | 3769 | 3994 | 3842 | 1200 | 1142 | 913.4 | 770.6 | 766.8 | 753.0 | 702.4 |
| 2 | 80.5 | 82.5 | 78.8 | 82.5 | 80.4 | 24.9 | 23.1 | 19.0 | 16.1 | 16.1 | 15.7 | 14.6 |
| 3 | - | - | - | - | - | 20.4 | 23.8 | 38.0 | 48.2 | 50.9 | 49.7 | 57.8 |
| 4 | 243.9 | 247.6 | 240.6 | 251.4 | 245.1 | 74.2 | 72.3 | 64.5 | 60.6 | 61.7 | 58.3 | 60.4 |
| 5 | 363.1 | 362.1 | 360.5 | 373.3 | 363.4 | 154.1 | 148.1 | 155.0 | 150.2 | 153.8 | 152.0 | 157.6 |
| 6 | - | - | - | - | - | 158.2 | 154.8 | 160.6 | 156.5 | 160.2 | 161.1 | 167.8 |
| 7 | - | - | - | - | - | 76.9 | 75.7 | 77.0 | 86.5 | 88.6 | 89.4 | 95.1 |
| 8 | - | - | - | - | - | 340.4 | 333.7 | 348.4 | 328.8 | 335.2 | 336.7 | 351.3 |
| 9 | - | - | - | - | - | 465.6 | 454.8 | 451.2 | 431.3 | 439.3 | 440.6 | 457.2 |
| 10 | - | - | - | - | - | 82.7 | 80.6 | 84.9 | 84.3 | 85.6 | 85.2 | 89.1 |
| 11 | - | - | - | - | - | 217.7 | 211.8 | 212.4 | 203.3 | 207.9 | 208.9 | 217.1 |
| 12 | - | - | - | - | - | 543.5 | 518.0 | 503.6 | 481.8 | 489.1 | 491.2 | 507.6 |
| 13 | - | - | - | - | - | 265.0 | 271.3 | 275.5 | 258.3 | 265.9 | 268.6 | 282.1 |
| 14 | - | - | - | - | - | 197.0 | 183.8 | 179.7 | 177.0 | 178.6 | 178.3 | 186.7 |
| 15 | - | - | - | - | - | 287.0 | 292.4 | 302.5 | 284.3 | 292.8 | 294.5 | 309.8 |
| 16 | - | - | - | - | - | 191.3 | 191.1 | 186.8 | 180.2 | 178.6 | 188.4 | 190.5 |
| 17 | - | - | - | - | - | 102.0 | 107.5 | 134.8 | 143.2 | 149.1 | 151.4 | 167.5 |
| 18 | - | - | - | - | - | 52.1 | 51.5 | 54.9 | 50.1 | 51.3 | 49.5 | 50.2 |
| 19 | 7.8 | 8.6 | 8.4 | 8.2 | 8.6 | 177.5 | 168.9 | 143.8 | 120.5 | 120.5 | 120.9 | 115.9 |

# APPENDIX G

# LABORATORY ANALYSIS RESULTS FROM THE ST. LAWRENCE CEMENT FACILITY TEST

by

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TRW Systems Group

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## APPENDIX G

## LABORATORY ANALYSIS RESULTS FROM THE ST. LAWRENCE CEMENT FACILITY TEST

### G.1 Summary

Analysis of the flue gas samples for organic composition gave the following results:

- Hydrocarbons were not detected in the samples of flue gas with detection limits ranging from 0.6 mg/m$^3$ to 0.009 mg/m$^3$.
- Low molecular weight chlorinated organic compounds such as methylene chloride, chloroform, and carbon tetrachloride were specifically searched for by gas chromatography with electron capture detection (ECD) and were generally not detected in most of the samples. Four samples indicated the possible presence of some of these compounds, but all at levels of less than 0.1 mg/m$^3$ of flue gas.
- Polychlorinated biphenyls were searched for by GC/ECD and GC/MS and were not found in any samples at the GC/MS detection limit of 3 μg/m$^3$ of flue gas.

Trace metal concentrations in the flue gases, as determined in the samples taken with the EPA sampling train, were all less than 10 μg/m$^3$, with the exception of lead in the WBC tests. The emission of lead during the WBC tests averaged 0.12 mg/m$^3$.

Analysis of the clinker product and discard dust samples for organic composition gave the following results:

- Hydrocarbons were not detected in solvent extracts of any of the clinker product or discard dust samples. The level of detection by GC/ECD was 5 μg/g of sample or lower.
- Polychlorinated biphenyls were not detected in any of the clinker or dust samples by GC/ECD. Detection limits for PCB's in the samples were typically 0.04 μg/g or better.

The inorganic character of the clinker products and electrostatic precipitator discard dusts was changed very little if at all by the addition

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of the chlorinated wastes to the SLC wet kiln process. Trace metal levels in the WBB and WBC test samples did not differ significantly from the baseline samples.

Analytical techniques selected for analysis of flue gas constituents which include vapours, condensables and particulate matter were gravimetric, IR, LRMS, GC, GC/MS, SSMS, ICPOES, and AAS. These were selected on the basis of sensitivity and selectivity criteria to enable identification of species in the flue gas at concentrations on the order of 0.1 mg/m$^3$, representing the threshold level of the most toxic species as defined by OSHA and other occupational health and safety organizations. Detection limits for many of the techniques extend to µg/m$^3$ levels. However, specific analyses to identify compounds below the level of interest, 0.1 mg/m$^3$, were not routinely performed. The techniques used were both qualitative and quantitative in nature, with an intended accuracy range of plus or minus a factor of two to three.

## G.2 Introduction

In cooperation with Environment Canada and the Ministry of Environment of Ontario, the United States Environmental Protection Agency supplemented the Canadian studies through participation in analyses of samples acquired from various streams during test burns of chlorinated hydrocarbons in the St. Lawrence Cement Co. wet process kiln. These analyses were performed by TRW Defense and Space Systems Group, Redondo Beach, California, under contract to the U.S. EPA. Samples were provided to TRW through the courtesy of the Ontario Research Foundation and St. Lawrence Cement Co., of Ontario, Canada.

Emphasis in the EPA sponsored work was directed toward analyzing for input waste residual compounds and by-products in the clinker (product), dust from the electrostatic precipitators, and the various component samples from the EPA Method 5 and ORF sorbent trap trains. These analyses were limited to the two test burns performed using chlorinated aromatic and polychlorinated biphenyl waste blends. In addition, background analytical work was accomplished on samples acquired during the two baseline tests in which the kiln was fired using only residual oil as a fuel. Analyses were also performed on the two waste blends. This work was done to supplement the Canadian laboratory results as well as to acquire additional evaluation data in accordance with U.S. EPA protocol used for ongoing chemical waste incineration test programs in the United States.

A brief economic analysis was made by St. Lawrence Cement Co. using data from both their own operations and from Chemtrol Pollution Services Inc. (Appendix E).

## G.3 Analysis Techniques

The purpose of the analyses performed on the samples from SLC was to identify and quantify:

- known hazardous species present from the waste as determined by pretest analysis of a sample of the waste material,
- secondary decomposition products (e.g., incomplete combustion products which are predictable), and
- other species found to be present but which are not predicted or otherwise expected.

A complete list of the samples received by TRW for analysis is given in Table G.1. This table shows what portion of the total sample collected by the trains was sent to TRW as well as the respective burns and test numbers for the received samples. The coding system used to uniquely identify each sample is shown in Figure G.1. These codes are used in subsequent tabulations of data and results.

The first step in the analytical approach involved various extraction and preparation procedures to separate the organic and inorganic constituents and/or to concentrate the samples in a suitable form for analysis. The extracts and concentrates were then analyzed by the techniques to be described in this section.

### G.3.1 Extractions and sample preparation

G.3.1.1 Solvent extracts received from ORF. With a few exceptions, solvent extractions for organic species were performed by ORF using pentane or hexane. Subsequently, ½ aliquots were received by TRW and combined according to the plan shown in Figure G.2. These combinations were performed because:

1) the ½ aliquots represent relatively small gas sample volumes, thus making constituent concentrations very low and difficult to measure, and

TABLE G.1. SUMMARY OF SAMPLES RECEIVED FROM EACH WASTE BURN

| Sample Description | Portion Received out of Total Sample | Burn and Test No. of Samples Origin | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | BLA | | | WBB | | | WBC | | | BLB | | |
| | | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| EPA Train | | | | | | | | | | | | | |
| • Probe rinse | | | | | | | | | | | | | |
| Filtered insolubles | All | | | | X | X | X | X | X | X | X | X | X |
| Solvent extract | 1/4 | | | X | X | X | X | X | X | X | X | X | X |
| Aqueous solution after filtration and extraction | All | | | | | | X | X | | | | | X |
| • Filter | | | | | | | | | | | | | |
| Solvent extract | 1/4 | | | X | X | X | X | X | X | X | X | X | X |
| Filter with particulate | All | | | | X | X | X | X | X | X | X | X | X |
| • Impingers | | | | | | | | | | | | | |
| Solvent extract | 1/4 | | | X | X | X | X | X | X | X | X | X | X |
| Aqueous solution after extraction | All | | | | | | X | X | | | | | X |
| ORF Train | | | | | | | | | | | | | |
| • In-stack filter | | | | | | | | | | | | | |
| Solvent extract | 1/4 | | | X | X | X | X | X | X | X | X | X | X |
| Filter with particulate | All | | | | X | X | X | X | X | X | X | X | X |
| • Probe rinse | | | | | | | | | | | | | |
| Filtered insolubles | All | | | | X | X | X | X | X | X | X | X | X |
| Solvent extract | 1/4 | | | X | X | X | X | X | X | X | X | X | X |
| Aqueous solution after filtration and extraction | All | | | | | | X | X | | | | | X |
| • NaOH impinger | | | | | | | | | | | | | |
| Solvent extract | 1/4 | | | X | X | X | X | X | X | X | X | X | X |
| Aqueous solution after extraction | All | | | | | | X | X | | | | | X |
| • Distilled water impinger | | | | | | | | | | | | | |
| Solvent extract | 1/4 | | | X | X | X | X | X | X | X | X | X | X |
| Aqueous solution after extraction | All | | | | | | X | X | | | | | X |
| • Chromosorb 102 sorbent tubes | 1/4 | | | | X | X | X | X | X | X | X | X | X |

| SAMPLE CODES CONSIST OF 3-5 SECTIONS | | | | |
|---|---|---|---|---|
| Burn | Sampling Train | Train Component Extracted | Any Special Preparation | Test No. |
| First Baseline on Primary Fuel - BLA<br>Waste Burn on Chlorinated Aromatics - WBB<br>Waste Burn on PCB Blend - WBC<br>Second Baseline on Primary Fuel - BLB | Standard EPA Method 5 Train - EPA<br>ORF Designed "Sorbent" Train - ORF | Filter/Insolubles - F<br>Probe Rinse - PR<br>Caustic Impinger - NAOH<br>Water Impinger - $H_2O$<br>Combined Impingers - I | Extracts of Acidified Solutions - AE | T1, T2, or T3 if sample is from only one test<br>Blank if sample is a combination of all three tests |

FOR EXAMPLE, ALL OF THE EXTRACTED SAMPLES FROM ONE WASTE BURN WOULD BE CODED AS FOLLOWS:

WBB-ORF-FE = Waste Burn B, ORF Train, Combined Filter Extracts from all three tests

WBB-ORF-PRE & NAOHE = Waste Burn B, ORF Train, Combined Probe Rinse and Caustic Impinger Extracts from all three tests

WBB-ORF-NAOH-AE-T3 = Waste Burn B, ORF Train, Extract of the acidified caustic impinger solution from Test 3

WBB-ORF-$H_2$OE = Waste Burn B, ORF Train, Combined Water Impinger Extracts from all three tests

WBB-EPA-FE & PRE = Waste Burn B, EPA Train, Combined Filter and Probe Rinse Extracts from all three tests

WBB-EPA-IE = Waste Burn B, EPA Train, Combined Impinger Extracts from all three tests

FIGURE G.1. TRW SAMPLE CODING SYSTEM

2) all three tests of each waste were performed at one nominal operating condition.

In general, following this plan, the organic concentrate obtained for each extracted sample type (e.g., filters, impingers, solids, etc.) from each of the two sampling trains were the combination of all three tests of each waste. Exceptions to this plan were the BLA and aqueous samples for which only one of the three test samples were received (see Table G.1). At no time were EPA train samples combined with ORF train samples.

Small aliquots (2-5 ml) were first taken of the "as received" extracts and set aside for analysis of volatile compounds that would be lost in the next step which was to concentrate the remaining solvent sample using Kuderna-Danish evaporators and a steam bath.

The solvent extracts of the probe rinses, in addition to being combined as in the plan shown in Figure G.2, were also combined with the sample (EPA train-filter, ORF train-first impinger) whose juxtaposition in the sampling train and similar physical characteristics permit the combination. The rinses of the EPA train were made of the glass probe liner in front of the filter. However, with the ORF train which only has a short nozzle in front of the in-stack filter, rinses were made of the 14 feet of probe and tubing between the filter and the first liquid impinger. The resulting solutions were filtered through standard filter paper and then extracted by ORF.

G.3.1.2 Solids, aqueous solutions, and filters. The solid samples were prepared for organic analyses by extraction in a Soxhlet apparatus for 24 hours with distilled-in-glass grade pentane. These extracts were concentrated with Kuderna-Danish evaporators to a 10 ml volume. Preparation of the solid samples for inorganic analyses consisted of a low-temperature plasma ashing to remove possible organic interferences.

Other samples for inorganic analysis also required some degree of preparation. Aliquots of the aqueous impinger and probe rinse samples were taken and acidified with nitric acid to stabilize any metals present. Each of the insoluble residues obtained by filtering the probe rinses was combined by ORF with its matching particulate filter for treatment as one sample. These insolubles/filter samples were plasma ashed and then

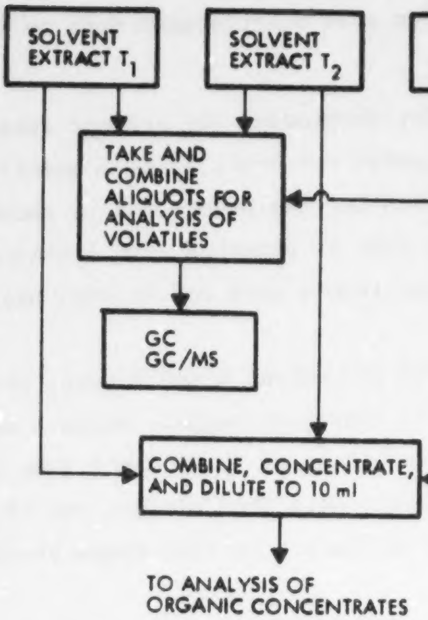
SOLVENT EXTRACT $T_1$
SOLVENT EXTRACT $T_2$
SOLVENT EXTRACT $T_3$
TAKE AND COMBINE ALIQUOTS FOR ANALYSIS OF VOLATILES
GC
GC/MS
COMBINE, CONCENTRATE, AND DILUTE TO 10 ml
TO ANALYSIS OF ORGANIC CONCENTRATES

FIGURE G.2. PLAN FOR THE COMBINATION OF ORF SOLVENT EXTRACTS

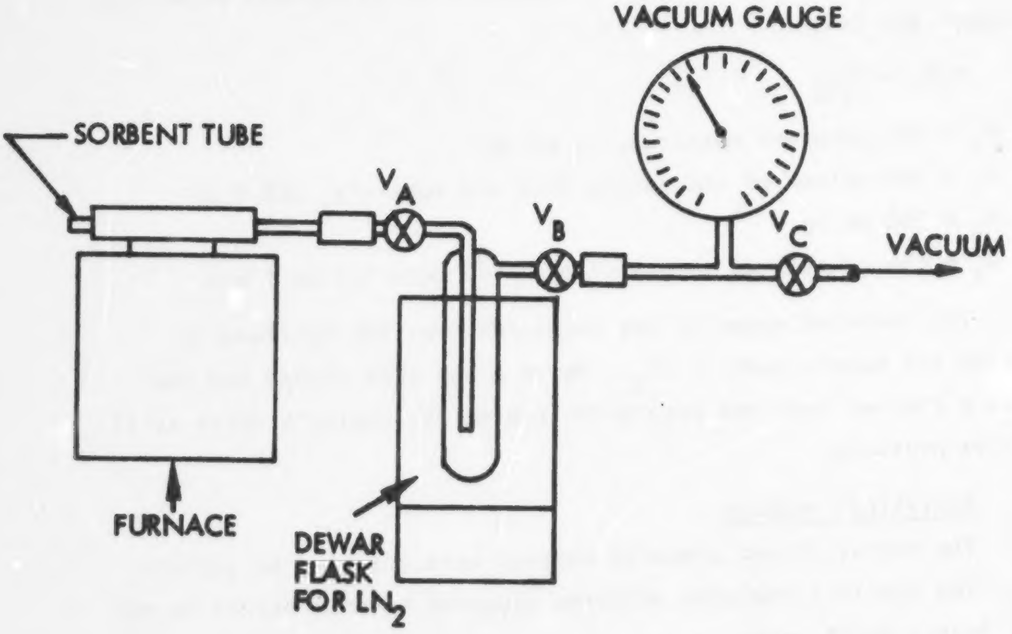
VACUUM GAUGE
SORBENT TUBE
$V_A$
$V_B$
$V_C$
VACUUM
FURNACE
DEWAR FLASK FOR $LN_2$

FIGURE G.3. DESORPTION SYSTEM FOR CHROMOSORB 102 TUBES

extracted by refluxing constant boiling aqua regia over the each sample for two hours. The resulting acid digests were made to 50 ml for analysis.

G.3.1.3 Sorbent tubes. The Chromosorb 102 sorbent tubes from the ORF sampling train were prepared for analysis by a quantitative desorption technique. The apparatus used for the desorption is shown schematically in Figure G.3. The sorbent tube is attached with a minimum length of Tygon tubing to a 20 ml glass sample bulb and is then heated in a small furnace to 185° ±10°C.

With valve A closed and valves B and C open, the sample bulb was evacuated and immersed in liquid nitrogen. Valve A was then opened for 30 minutes to allow the contents of the sorbent tube to transfer to the sample bulb. Valves A and C were then closed, the $LN_2$ flask removed, the sample bulb allowed to equilibrate to room temperature, and the pressure recorded.

The volume of the entire manifold system, including each sample bulb, was carefully calibrated and on the average was 68.8 cc. With this information and the recorded pressure (assuming the temperature to be constant), the volume of the material desorbed was calculated according to the ideal gas law:

$$P_1V_1 = P_2V_2$$

where: $P_1$ = the pressure measured, in mm Hg
$V_1$ = the volume of the sample bulb and manifold, ~68.8 cc
$P_2$ = 760 mm Hg
$V_2$ = the calculated volume of desorbed material at 1 atm.

The desorbed material was recovered from the manifold by reimmersing the sample bulb in $LN_2$. Valve B was then closed and the sample bulb removed from the desorption system for analysis while still at negative pressure.

### G.3.2 Analytical methods

The extracted and prepared samples were analyzed by various methods. The specific analyses selected depended to some extent on the samples' forms, which were:

For Inorganics

- Solids
- Aqueous and acid solutions

For Organics

- Aliquots of the neat solvent extracts
- Concentrates of the solvent extracts
- Desorbed materials from the sorbent tubes

G.3.2.1 Analyses for inorganics. The inorganic composition of the solid samples was determined by spark source mass spectrophotography (SSMS) with electronic detection, which will detect elements present down to a concentration of 1 ppm. This SSMS technique has an accuracy from 100-500% and will survey the sample for all the elements except gases (i.e., H, N, O, He, Ne, Ar, Kr, Xe, and Rn) and Hg because of its high volatility. Other elements with appreciable volatilities, such as Be and Se, have far reduced accuracies in this analysis.

The aqueous and acid solutions were first surveyed for metals by inductively coupled argon plasma optical emission spectroscopy (ICPOES). The ICPOES analysis determines 32 elements, including most of the toxic elements of interest in the program, down to ppb levels, with an accuracy of 100-200%. The purpose of this survey was primarily to check that the metals in the test samples were present in approximately the same amounts relative to each other as they were in the waste material. Those elements which, from the results either of the ICPOES survey or of the analysis of the waste material, seemed to be present at potentially toxic levels, were determined quantitatively by atomic absorption spectrometry (AAS). The sensitivity of this method varies from approximately 1.0-0.001 ppm for the elements which were determined, with an accuracy between 10-50%.

G.3.2.2 Analyses for organics. Organic constituents of the test samples were determined by a combination of the following techniques:

- infrared spectrometry (IR);
- gas chromatography (GC) with either an electron capture (EC) or flame ionization detector (FID);
- low resolution mass spectrometry (LRMS);
- combined gas chromatography/mass spectrometry (GC/MS).

The aliquots of the neat solvent extracts were analyzed only for volatile organochlorine compounds. EC/GC was used for this analysis and the samples were compared to standards of $CH_2Cl_2$, $CHCl_3$, and $CCl_4$ as well as the original waste material. The column was 183 cm x 0.635 cm o.d., glass, 1.5% OV 17 and 1.95% QF-1 on Chromosorb WHP.

The concentrates of the solvent extracts were analyzed to identify the less volatile compounds that would not be lost by evaporation of the extract. An aliquot of each sample was first taken and evaporated in a clean, 7 ml weighing bottle at ambient conditions to remove the solvent. The residue was then weighed on a micro balance to 0.001 mg and scanned by IR as an evaporated thin film. The sample was returned to the weighing bottle and stored for use in the LRMS analysis. To obtain an LRMS spectra, the sample was rinsed into the glass vessel for the solids probe inlet system and the solvent evaporated again at ambient conditions. The IR and LRMS analyses yield qualitative information about the classes or types of compounds (e.g., hydrocarbons, phenols, POM's, etc.) present as well as an idea of the complexity and toxic nature of the concentrated sample.

The sensitivity of the LRMS solids probe technique for specific compounds in an organic matrix can be estimated even though the mass spectrometer is not strictly considered a quantitative instrument. At typical mass spectrometer operating pressures of $10^{-6}$ torr, the relative volatility of organic materials at normal solids probe temperatures (100-250°C) is not an important factor. That is, the volatilities of materials of interest are sufficiently high for adequate detection. The solids probe of the mass spectrometer is in such close proximity to the ionizer that sample diffusion does not significantly reduce sensitivity. Previous experience and contacts with other laboratories using similar equipment indicate that if 10 micrograms of an organic compound is present in a solids probe along with other material, it will be detected to the extent that the ten or more strongest fragment peaks will be recorded. Since the typical weight of sample placed in the solids probe is 1 milligram, the required weight percentage of a given organic compound to be detected in an organic matrix is approximately one percent. Therefore, any compounds not detected by LRMS were assumed to be present at less than one percent levels.

The organic compounds in the extract concentrates were separated and quantified by GC using both flame ionization and electron capture detection. Columns and GC conditions are given below:

Flame ionization detection

- Varian 1860, dual differential FID
- Columns: dual, 183 cm x 2 mm i.d., stainless steel, 3.5% OV-17 on 100/120 mesh Chromosorb WHP
- Temperatures: column, ambient for 5 minutes, then ambient to 275°C at 10°C/min; detector, 275°C; injector, 250°C.
- Flow rate: helium carrier at 30 ml/min; hydrogen at 30 ml/min.; air, 300 ml/min.
- Attenuation: $1 \times 10^{-10}$ a/mv

Electron capture detection

- Tracor MT-150, $^{63}$Ni single ECD
- Column: 183 cm x 0.4 cm i.d., glass, 1.5% OV-17 and 1.95% QF-1 on 80/100 mesh Chromosorb WHP
- Temperatures: column, 200°C; detector, 225°C; injector 225°C.
- Flow rates: pre-purified $N_2$ carrier through column at 60 ml/min.; detector purge at 40 ml/min.
- Polarizing voltage: 14V; bucking range $-2 \times 10^{-8}$; input attenuation, $10^2$; output attenuation, X2 to X64.

## G.4 Analytical Data

Data obtained from the various analyses performed will be presented in this section in the following order:

Chlorinated Hydrocarbon Wastes Tested

- Chlorinated Aromatics
- Polychlorinated Biphenyls (PCBs)

Samples Obtained from the EPA and ORF Sampling Trains

- Organic Constituents
- Inorganic Characterization

Solid Residues and Effluents from the SLC Kiln Process

- Clinker Products
- Electrostatic Precipitator Discard Dusts

### G.4.1 Chlorinated hydrocarbon wastes tested

Samples of the chlorinated wastes burned at St. Lawrence Cement were taken by ORF from the liquid waste feed tank on each day of testing. Composites of these were sent to TRW. The analyses used to characterize the wastes and determine the expected compounds of interest in the test burn samples were:

- thermal content - gross heat of combustion;
- viscosity;
- specific gravity;
- loss on ignition (LOI);
- C, H, N, S, and halogens;
- infrared spectroscopy (IR);
- gas chromatography/mass spectroscopy (GC/MS); and,
- spark source mass spectroscopy (SSMS).

G.4.1.1 Primary fuel. In addition to the two wastes, a sample of the primary fuel, bunker "C" oil, was also received. Of the analyses listed above only the gross elemental determination (C, H, N, S, and halogens) and a trace metal scan by X-ray fluorescence (XRF) were performed on the oil. Physical properties were not determined since they are fairly standard, and accurate compound identification was not necessary since the background of compounds contributed by burning the bunker "C" oil as fuel can best be determined by analysis of the combustion test samples from the baseline burn.

The elemental determination on the oil gave the following results:

- 86.87% C
- 9.89% H
- C.36% N
- 2.62% S
- 0.05% Cl (total halogens as chlorine).

The XRF scan detected six elements at the levels listed below:

| Element | Approximate Concentration (ppm) |
|---|---|
| Si | >500 |
| P | 50-500 |
| Ni | 5-50 |
| V* | 5-50 |
| Ca | <25 |
| Ti | <5 |

G.4.1.2 Chlorinated aromatics. The aromatic waste was a dark brown, low viscosity liquid that was visually free of sediment. The measured physical characteristics were:

- thermal content - 5170 kcal/kg (9310 Btu/lb);
- viscosity - 1.09 centistokes at 38°C (100°F);
- specific gravity - 1.281 at 16°C (60°F);
- LOI - 99.98%.

Elemental analyses performed showed the following composition:

- 44.00% C
- 3.48% H
- 0.028% N
- 0.019% S
- 49.10% Cl (total halogens as chlorine).

Analytical techniques used to determine the organic composition included IR and GC/MS.

IR

The IR spectrum indicated the waste to be composed primarily of aromatic hydrocarbons as well as aliphatic alkanes and alkenes with a strong response in the 600-800 $cm^{-1}$ region which can correspond to C-Cl bonding. No indication of any other functional groups such as phenols, ethers, or amines was found. Comparison of the waste spectrum with spectra from the Sadtler indices for the compounds found by GC/MS, showed the principle constituent to be o-chlorotoluene, the most characteristic peak of which is a strong, sharp peak at 750 $cm^{-1}$.

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*Element is potentially toxic - OSHA TLV of <1 $mg/m^3$ for an eight-hour exposure.

GC/MS

Chromatographic separation was carried out on a Finnigan GC/MS system using two columns. One was Chromosorb 101, temperature programmed from 30° - 220°C at 10°C/min, and the other was OV-17 temperature programmed from 30° - 275°C at 10°C/min. The compounds shown in Table G.2 were identified and their concentrations calculated based on relative peak areas found from both columns and assuming equal response to the total ion monitor of the Finnigan instrument. These results reflect the fact that, in the course of performing the tests at SLC, the waste feed tank was not emptied between wastes. Thus, the material for the "aromatic" burns contains ∿33% chlorinated aliphatics carried over from the previous burn (as a cost savings to the program, TRW did not plan to analyze samples from the chlorinated aliphatics burn). The primary constituent of the aromatic waste is chlorotoluene (52.5%) with the remainder made up of three other chlorinated aromatics: dichlorotoluene, octachlorocyclopentene, and octachloronaphthalene.

TABLE G.2. ORGANIC COMPOSITION OF AROMATIC WASTE BY GC/MS

| Compound | Estimated Concentration (% w/w) |
|---|---|
| Acetone | 1.6 |
| Methylacetate | 0.3 |
| Dichloromethane | 0.4 |
| Chloroform | 11.1 |
| Carbon Tetrachloride | 13.9 |
| Dichloroethane | 3.1 |
| Trichloroethane | 2.5 |
| Tetrachloroethane | 0.4 |
| Trichloroethylene | 1.0 |
| Toluene | 1.0 |
| Chlorotoluene | 52.5 |
| Dichlorotoluene | 4.6 |
| Dimethyl Benzene (Xylene) | 0.9 |
| Octachlorocyclopentene | 3.7 |
| $C_{10}Cl_8$ (Octachloronaphthalene) | 3.0 |

## SSMS

Trace metals in the chlorinated aromatic waste were determined by spark source mass spectroscopy (SSMS). The waste was first ashed by a sulphated dry method. A very small amount of ash, 0.014%, was obtained of which the major elements were Ba, Fe, Na, P, S, Si, and Ti (the sulphur most likely represents the contribution from the $H_2SO_4$ added during ashing). Other elements detected by SSMS down to 1 ppb are shown in Table G.3. This analysis was performed to determine what potentially toxic elements might have been present in the waste at high enough concentrations to warrant quantitative examination of the flue gas test samples. Given the semi-quantitative nature of the data, the SSMS results should not be construed as a quantitative characterization of the waste material.

TABLE G.3. TRACE METALS IN THE CHLORINATED AROMATIC WASTE BY SSMS

| Element | Approximate[a] Concentration (ppm) | Element | Approximate[a] Concentration (ppm) |
|---|---|---|---|
| Al | 0.7-1.5 | Sn | 0.008 |
| Ca | 0.7-1.5 | Zr | 0.008 |
| Cu | 0.7-1.5 | V[b] | 0.007 |
| Mg | 0.7-1.5 | As[b] | 0.006 |
| Zn | 0.7-1.5 | Ag | 0.003 |
| K | 0.6 | Cd[b] | 0.002 |
| Cr[b] | 0.4 | Ce | 0.002 |
| Pb[b] | 0.3 | La | 0.002 |
| Mn | 0.07 | Sb[b] | 0.002 |
| Hg[b,c] | 0.07 | Be[b] | 0.001 |
| Sr | 0.06 | Bi | 0.001 |
| Pt | 0.05 | Ge | 0.001 |
| B | 0.05 | Li | 0.001 |
| Co[b] | 0.05 | Rb | 0.001 |
| Ni | 0.03 | Se[b] | 0.001 |
| W | 0.01 | Sm | 0.001 |
| Mo | 0.008 | Yb | 0.001 |

[a] The accuracy of this technique ranges from 100 to 500 percent.

[b] Potentially toxic metals - OSHA TLV of $<1$ mg/m$^3$ for an eight-hour exposure.

[c] Hg was determined by a highly quantitative atomic fluorescence technique.

G.4.1.3 Polychlorinated biphenyls (PCB's). The PCB waste was a medium brown, low viscosity liquid with fine suspended particulate that tended to float to the top and cake out on the sides of the container. The measured characteristics were:

- thermal content - 6,710 kcal/kg (12,083 Btu/lb);
- viscosity - 5.87 centistokes at 38°C (100°F);
- specific gravity - 1.196 at 16°C (60°F);
- LOI - 99.90%

Elemental analyses performed showed the following composition:

- 57.94% C
- 5.23% H
- 0.018% N
- 0.12% S
- 33.60% Cl (total halogens as chlorine).

The analytical techniques used to determine the organic composition of the waste were IR and GC/MS.

IR

The IR scan showed strong peaks at 1100 $cm^{-1}$ and 1450 - 1480 $cm^{-1}$ which are characteristic of biphenyls, and a peak at 750 $cm^{-1}$ indicative of remaining o-chlorotoluene in the waste. Other small peaks in the spectrum matched those in the aromatic waste IR scan which substantiates the GC/MS results discussed below.

GC/MS

Analysis of the PCB waste was performed by the same GC/MS methods and conditions as for the aromatic waste, and the compounds that were identified are shown in Table G.4. The PCB waste composition showed the effect of previous waste material left in the feed tank. It was composed of 12% chlorinated aliphatics, 33% chlorinated aromatics, and 45% PCBs. There were 22 separate PCB compounds identified including several isomers of each of the multiple chlorinated biphenyls.

SSMS

Trace metals in the PCB waste were determined by SSMS. The waste was first ashed by a sulphated dry method. A small amount of ash, 0.15%,

TABLE G.4. ORGANIC COMPOSITION OF PCB WASTE BY GC/MS

| Compound | Estimated Concentration (% w/w) |
|---|---|
| Water | 0.7 |
| Acetone | 1.3 |
| Methylacetate | 0.5 |
| Methanol | 0.4 |
| Chloroform | 1.4 |
| Carbon Tetrachloride | 6.8 |
| Ethanol | 5.2 |
| Dichloroethane | 0.6 |
| Trichloroethane | 0.7 |
| Hexachloroethane | 0.2 |
| Trichloroethylene | 1.6 |
| Tetrachloroethylene | 0.2 |
| Xylenes | 2.3 |
| Toluene | 1.0 |
| Chlorotoluene | 17.2 |
| Dichlorotoluenes | 2.4 |
| Trichlorotoluenes | 3.3 |
| Octachlorocyclopentene | 4.0 |
| Chlorobiphenyl | 0.5 |
| Dichlorobiphenyls | 8.4 |
| Trichlorobiphenyls | 15.5 |
| Tetrachlorobiphenyls | 11-15 |
| Pentachlorobiphenyls | 2-6 |
| Hexachlorobiphenyls | 1-2 |
| Heptachlorobiphenyls | 0.5 |
| Octachlorobiphenyls | 0.2 |
| Di-n-octyl or Di-ethyl Hexyl Phthalate | 4.0 |
| $C_{10}Cl_8$ - Octachloronaphthalene | 2.5 |

was obtained of which the major elements were Fe, Na, P, Pt, and Si. Other elements detected by SSMS down to 1 ppb are shown in Table G.5. This analysis was performed to determine what potentially toxic elements might have been present in the waste at high enough concentrations to warrent quantitative examination of the flue gas test samples. Given the semi-quantitative nature of the data, the SSMS results should not be construed as a quantitative characterization of the waste material.

### G.4.2 Samples obtained from the EPA and ORF sampling trains

Samples obtained by the two trains from the WBB, WBC, and BLB tests were received for analysis. A list of the samples derived by ORF

TABLE G.5. TRACE METALS IN THE PCB WASTE BY SSMS

| Element | Approximate[a] Concentration (ppm) | Element | Approximate[a] Concentration (ppm) |
|---|---|---|---|
| K | 7-15 | Se[b] | 0.1 |
| Zn | 7-15 | Sr | 0.07 |
| Cu | 7 | Hg[b,c] | 0.06 |
| S | 5 | Cd[b] | 0.05 |
| Mg | 5 | Th | 0.02 |
| Al | 4 | La | 0.01 |
| Ni | 4 | Nb | 0.01 |
| Mo | 3 | Bi | 0.009 |
| Ba[b] | 2 | Li | 0.009 |
| Ti | 2 | Rb | 0.006 |
| B | 1 | Ta | 0.004 |
| Ca | 1 | Au | 0.003 |
| W | 1 | Nd | 0.003 |
| Cr[b] | 0.8 | Hf | 0.002 |
| Pb[b] | 0.8 | Sm | 0.002 |
| V[b] | 0.7 | Be[b] | 0.001 |
| Ag | 0.6 | Dy | 0.001 |
| Mn | 0.5 | Ga | 0.001 |
| Sb[b] | 0.5 | Ge | 0.001 |
| Sn | 0.5 | Pr | 0.001 |
| As[b] | 0.2 | Sc | 0.001 |
| Zr | 0.2 | U | 0.001 |
| Co[b] | 0.1 | | |

[a] The accuracy of this technique ranges from 100 to 500 percent.

[b] Potentially toxic metals - OSHA TLV of <1 mg/$m^3$ for an eight-hour exposure.

[c] Hg was determined by a highly quantitative atomic fluorescence technique.

from each train was presented in Table G.1. All of these samples were scheduled to be analyzed until, in early April, ORF's review of their analytical data brought them to conclude that the solvent extracts of the BLB samples had been contaminated with PCB waste material [G.1] which was confirmed by the analyses at TRW. The contamination appeared to have occurred before the split of the samples into ¼ aliquots. In view of this development, analysis of the BLB solvent extract samples was discontinued and extracts from a BLA test were sent as replacements.

However, there was no evidence of a contamination problem with the remaining BLB samples. Thus, the filters, probe rinse insolubles, aqueous solutions, and Chromosorb 102 sorbent tubes from the BLB tests were analyzed for a background reference to the corresponding WBB and WBC samples.

All of the test samples were coded for ease of reference. The coding used was presented in Figure G.1, which also showed the combination of the probe rinse samples with other appropriate samples. The reasons and methods for combining the probe rinses with either the filter (for the EPA train) or impinger (for the ORF train) samples, as well as the preparation and analytical techniques for all the samples were described in Section G.3.

Where constituents found in the test samples are reported as concentrations in the effluent gas, the sample gas volumes needed for the calculations were taken from Section 5.3 of the report. Volumes for the ORF train were taken from Table 4, and volumes for the EPA train from Table 7.

G.4.2.1 Organic constituents. Samples for the analysis of organic composition were in the form of:

- aliquots of the neat solvent extracts;
- concentrates of the solvent extracts;
- residues from the evaporation of the extract concentrates; and
- desorbed materials from the sorbent tubes.

These samples were first surveyed for their qualitative nature by gravimetric, infrared spectrometry (IR), and low resolution mass spectrometry (LRMS) techniques. Quantitative determinations and analysis for specific compounds, such as chlorinated hydrocarbons and PCB's, were then performed by gas chromatography (GC) and combined gas chromatography/mass spectrometry (GC/MS). The results obtained from all of these analyses are presented in the following paragraphs. The methods themselves are described in Section G.3.

Qualitative data. The purpose of the qualitative or survey analysis was to identify any material in the samples which were not present in the original waste, and therefore were not expected. In addition, this survey analysis searched for secondary or incomplete combustion products which would result from the waste being converted to compounds other than $CO_2$, $H_2O$, and HCl. The qualitative data will be described in two groups: 1) Extract concentrate residues, and 2) material desorbed from the sorbent tubes.

1) Extract concentrate residues - The results of these qualitative analyses on the residues, obtained by evaporating aliquots of the solvent extract concentrates, are summarized and presented in Table G.6. This table includes:

- The identification of the extract samples according to the coding shown in Figure G.1. This coding shows how certain related samples have been combined.
- The Sample/Aliquot Ratio shows the total volume of extract prepared by ORF in the numerator and the volume received by TRW in the denominator. One-fourth of each extract was sent to TRW.
- The amount of residue found in TRW's portion of the total extract is expressed as milligrams (mg). Values have been corrected for appropriate blanks.
- The Total Residue is that amount (in mg) of residue found in TRW's portion, multiplied by the Sample/Aliquot Ratio. This value is indicative of what may be found in the total extract if analyzed by the same procedures.

Inspection of the IR and LRMS data revealed that the only materials detected in the evaporated residues of the various extracts (except for the contaminated BLB samples) were silicones, hydrocarbon oils, fatty acids or fatty acid esters, and phthalic acid esters.

These same materials were also present in the blank and control samples; their concentrations vary from sample to sample as estimated by LRMS. These materials, as classes of compounds, are not toxic and would not be considered an emissions hazard even if they were present in much higher concentrations. These materials are not believed to have come from the combustion gas. Samples from the EPA train did not show increased levels of these materials consistent with more than ten-fold sample volumes.

In the analysis of trace organics, it becomes very difficult to completely avoid these ubiquitous oils, plasticisers, lubricants, antioxidants,

## TABLE G.6. SUMMARY OF ORGANIC QUALITATIVE SURVEY ANALYSES OF SAMPLE EXTRACTS

| Sample Identification | Total Extract (ml) / TRW Aliquot (ml) | Survey Residue Found in TRW Aliquot (mg) | Total Residue (mg, corrected for Aliquot Factor) |
|---|---|---|---|
| **Baseline Burn A** | | | |
| BLA-ORF-FE-T3 | 200/50 | 3.23 | 12.92 |
| BLA-ORF-PRE+NAOHE-T3 | 200/50 | N/D[b] | N/D (<1.00) |
| BLA-ORF-$H_2O$E-T3 | 100/25 | N/D[b] | N/D (<2.68) |
| BLA-EPA-PRE+FE-T3 | 300/75 | 0.12 | 0.48 |
| BLA-EPA-IE-T3 | 100/25 | 2.09 | 8.36 |
| **Baseline Burn B** | | | |
| BLB-ORF-FE | 600/150 | 0.34 | 1.36 |
| BLB-ORF-PRE+NAOHE | 600/150 | N/D[b] | N/D (<1.00) |
| BLB-ORF-$H_2O$E | 300/75 | 0.50 | 2.00 |
| BLB-EPA-PRE+FE | 900/225 | 0.48 | 1.92 |
| BLB-EPA-IE | 300/75 | 0.04 | 0.16 |
| **Waste Burn B** | | | |
| WBB-ORF-FE | 600/150 | 0.07 | 0.28 |
| WBB-ORF-PRE+NAOHE | 400/100 | N/D[b] | N/D (<1.00) |
| WBB-ORF-$H_2O$E | 200/50 | N/D[b] | N/D (<2.68) |
| WBB-ORF-NAOH-AE-T3 | N/A[c] | 0.28 | 1.12 |
| WBB-EPA-PRE+FE | 900/225 | 1.50 | 6.00 |
| WBB-EPA-IE | 300/75 | 11.18 | 44.72 |
| **Waste Burn C** | | | |
| WBC-ORF-FE | 600/150 | 0.58 | 2.32 |
| WBC-ORF-PRE+NAOHE | 600/150 | N/D[b] | N/D (<1.00) |
| WBC-ORF-$H_2O$E | 300/75 | 14.83 | 59.32 |
| WBC-ORF-NAOH-AE-T1 | N/A[c] | 0.23 | 0.92 |
| WBC-EPA-PRE+FE | 900/225 | 1.12 | 4.48 |
| WBC-EPA-IE | 300/75 | 6.25 | 25.00 |

[a] There is no significant difference in the results between test runs. The materials in the residues are not believed to have come from the combustion gas.

[b] N/D = Not detected at levels higher than the blank.

[c] N/A = Not applicable; the total caustic impinger contents from one test were used.

etc., that can enter the test matrix in very small amounts despite the most careful and extensive preparation of equipment and selection of reagents. One cannot be sure whether the source of these materials is the hardware, the reagents, the samples themselves, or a combination of these. A large number of blank and control samples might have distinguished the source, but due to the noncritical nature of the materials, such an examination was clearly not warranted.

It was pointed out that the survey analysis of the BLB samples known to contain PCB's [G.1] did, in fact, reveal their presence. Evidence of PCB,s was clearly shown in the LRMS data for the following BLB samples:

- ORF train, combined probe rinse extracts and caustic impinger extracts;
- ORF train, water impinger extracts;
- EPA train, combined probe rinse extract and filter extract.

Since these PCB's were found only as estimated minor constituents in samples whose total weights were less than one milligram, the ability of the mass spectrometer to detect these small quantities was clearly established. The LRMS procedures can usually detect 10 micrograms, or about one percent of a typical 1 milligram sample. The presence of a specific compound in an organic matrix is not normally detected by IR with adequate certainty unless present at 10 percent or higher. The sensitivity and detection limits of these techniques were discussed in Section G.3.2.

It is stressed that chlorinated species were specifically searched for in all of these residue samples and none were found except for in the contaminated BLB samples described above.

2) Materials desorbed from the sorbent tubes - The Chromosorb 102 sorbent tubes from the ORF sampling train were thermally desorbed to recover the collected sample according to the procedure described in Section G.3.1. The desorbed gases were then analyzed qualitatively by LRMS using a gas inlet system. The conclusions drawn from reduction and interpretation of the LRMS data were that all of the sorbent tubes contained essentially the same types of materials; however, the relative amounts of these constituents did appear to vary from sample to sample.

Although the LRMS is a qualitative technique, estimates can be made through inspection of the data to provide an indication as to whether a species is present as a trace, minor, moderate, or major component. Such a summary for the six selected sample sorbent traps that were analyzed is presented in Table G.7. An unused sorbent trap was also analyzed by the same procedure to estimate background contributions by the Chromosorb 102. Unfortunately a leak in the system resulted in the loss of sample and, therefore, usable data. Only carbon dioxide was seen in the mass spec data at greater than trace levels.

The volatile compounds removed from the sorbent traps and collected in the gas sample bulbs were largely the oxygen, nitrogen, carbon dioxide, and water that are the usual species found in combustion gases. The remainder of the compounds detected were those that could indicate incomplete combustion, or possibly the formation of other compounds. The levels at which these remaining compounds could be present were estimated on the basis of LRMS instrument response for key peaks attributed to these trace residual organics. These estimates indicated that the $C_1$ to $C_5$ hydrocarbons present as a major component of these trace residual organics could be present in the sampled combustion gases in the 1 to 10 ppm range. The minor or trace components of these trace organics were believed to be present at very much lower levels.

A summary of the LRMS peak patterns observed in the spectra of the desorbed gases and the compounds assigned to these patterns is given in Table G.8.

Quantitative data. Quantitation of the compounds detected and identified in the test samples was performed by GC and GC/MS techniques.

1) Extract concentrates - The chromatography with flame ionization detection was performed chiefly to analyze organic species. It should be noted that the FID is quite sensitive to chlorinated hydrocarbons as long as chlorination is not complete. At the electrometer settings used, the sensitivity, or the minimum detectable quantity, was 0.002 μg/μl as benzene, naphthalene, or Aroclor 1232.

The chief result of the analyses using the FID was that none of the concentrated samples showed peaks other than those found in the

TABLE G.7. APPROXIMATE CONSTITUENT LEVELS OF TRACE VAPOURS DESORBED FROM SORBENT TUBE SAMPLES BY LRMS

| Sorbent Tube Sample | Constituent Level[a] | | | | | | |
|---|---|---|---|---|---|---|---|
| | $C_{1-5}$ Hydrocarbons | Nitromethane | NO, $NO_2$, and Possibly Ethanol | Benzene | Methyl Chloride | Substituted Benzene | Methyl Siloxane |
| WBB-T1 | Minor | Trace | Trace | Trace | ND[b] | ND | Major |
| WBB-T2 | Major | Minor | Major | Moderate | Moderate | Trace | Minor |
| WBC-T1 | Major | Minor | Major | Minor | ND | Trace | Minor |
| WBC-T2 | Major | Minor | Major | Moderate | ND | Trace | Trace |
| BLB-T1 | Major | Moderate | Moderate | Major | ND | Trace | Trace |
| BLB-T2 | Major | Minor | Moderate | Moderate | ND | Trace | Trace |

[a] The range of trace to major levels represents 0.1-10 ppm concentrations in the flue gas.

[b] ND - Not Detected.

TABLE G.8. SUMMARY OF THE INTERPRETATION OF LRMS SPECTRA FOR TRACE VAPOURS DESORBED FROM SORBENT TUBE SAMPLES

| Peak Pattern (Peaks at Atomic Mass Units (AMU)) | Assignment |
|---|---|
| 15 | Methyl group, $CH_3$ |
| 16 | Methane, $CH_4$ |
| 17, 18 | Water |
| 27, 29, 41, 43, 55, 57 | $C_2$-$C_5$ hydrocarbons |
| 14, 16, 28, 32 | Nitrogen/oxygen |
| 44 | $CO_2$ |
| 30, 46, 61 | Possibly nitromethane $CH_3NO_2$* |
| 30, 46 | NO, $NO_2$* and/or ethanol |
| 78, 50, 51, 52 | Benzene |
| 50, 52, 15 | Methyl chloride $CH_3Cl$ |
| 91 | Substituted benzene ring (e.g., toluene) |
| 147, 207, 281 | Methyl siloxane |

*The 30 AMU peak was very large and it is believed that nitric oxide, nitrogen dioxide, ethanol and nitromethane may have all contributed to it.

solvent controls. Consequently, a "less than" value was assigned in terms of benzene for the analysis of hydrocarbons, or Aroclor 1232 for the analysis of chlorinated organics. The results are given in Table G.9.

The values presented in Table G.9 were derived in the following manner. The sample labeled WBB-EPA-FE+PRE, for example, totaled 225 ml as received. A 213 ml portion of this sample was concentrated to 10 ml in a Kuderna-Danish evaporator. The chromatogram of the concentrated sample showed no peaks other than solvent. Since the aromatic waste contained considerable chlorinated hydrocarbons, quantitation as Aroclor 1232 was considered appropriate.

Thus, WBB-EPA-FE+PRE contained <0.002 µg/µl of species as Aroclor 1232. The amount of material in the entire received sample volume of 225 ml was determined. This value was multiplied by four, since only one-quarter

TABLE G.9. RESULTS AND DETECTION LIMITS FROM GC/FID ANALYSIS OF THE CONCENTRATED EXTRACTS

| Sample ID | ng/μl as Halocarbon[d] | Volume of Sample (ml)[a] | Aliquot Factor[b] | Fraction of Sample[c] | Volume of Sample Gas, Std. $m^3$ | Concentration in Flue Gas ($mg/m^3$) |
|---|---|---|---|---|---|---|
| BLA-EPA-FE+PRE-T3 | 0.052 | 75 | 67/20 | 1/4 | 3.76 | 0.001 |
| -IE-T3 | 0.26 | 25 | 21/10 | 1/4 | 3.76 | 0.003 |
| -ORF-FE-T3 | 0.26 | 50 | 46/10 | 1/4 | 0.32 | 0.04 |
| -$H_2$OE-T3 | 0.061 | 25 | 21/10 | 1/4 | 0.32 | 0.09 |
| -PRE+NAOHE-T3 | 0.21 | 50 | 42/20 | 1/4 | 0.32 | 0.06 |
| WBB-EPA-FE+PRE | ND(<0.0038)[e] | 225 | 213/10 | 1/4 | 9.62 | ND(<0.00002) |
| -IE | 0.89 | 75 | 63/10 | 1/4 | 9.62 | 0.004 |
| -ORF-FE | 0.12 | 150 | 138/10 | 1/4 | 0.83 | 0.006 |
| -$H_2$OE | 0.26 | 50 | 42/10 | 1/4 | 0.83 | 0.02 |
| -PRE+NAOHE | 0.053 | 100 | 42/10 | 1/4 | 0.83 | 0.003 |
| WBC-EPA-FE+PRE | 0.019 | 225 | 213/10 | 1/4 | 9.97 | 0.00008 |
| -IE | (lost) | 75 | 63/10 | 1/4 | 9.97 | (lost) |
| -ORF-FE | ND(<0.0038) | 150 | 138/10 | 1/4 | 0.73 | ND(<0.00002) |
| -$H_2$OE | ND(<0.0038) | 75 | 63/10 | 1/4 | 0.73 | ND(<0.00002) |
| -PRE+NAOHE | 0.26 | 150 | 138/10 | 1/4 | 0.73 | 0.015 |

[a] Volume of sample received by TRW.

[b] Aliquot Factor: for example 67 ml of the 75 ml BLA-EPA-Fe+PRE sample received was concentrated to 20 ml for analysis.

[c] Fraction of Sample: All samples received by TRW were 25% of the total sample.

[d] The instrument was calibrated with Aroclor 1232. However, the Aroclor peak pattern was not found in any sample chromatogram. High sensitivity GC/MS (3μg/$m^3$ of flue gas) did not detect any chlorinated species in samples WBC-ORF-FE and WBC-ORF-H2OE.

[e] ND = Not detected. Values in parentheses indicate the detection limits.

of the whole sample was divided by the volume, in $m^3$, of gas sampled. A concentration value of <0.009 $mg/m^3$ in the flue gas was thus derived for the sample WBB-EPA-FE+PRE.

Since the minimum detectable quantity is constant and since both the volume of gas sampled and the volume of extract vary, this method of calculation gives different values of $mg/m^3$. It must be stressed that these analyses showed no species other than solvent.

Since the ECD is much more sensitive to polychlorinated species than the FID, the analyses using electron capture detection were performed to determine polychlorinated compounds below the level that could be detected by the FID analyses. At the electrometer setting used on the electron capture detector, the minimum detectable quantities for typical species of interest were:

- Aroclor 1232: 0.0038 ng/μl
- Naphthalene: 0.066 μg/μl
- Benzene: 0.11 μg/μl.

The most noteworthy result of the GC analyses using the ECD was that none of the concentrated extracts showed peak patterns corresponding to those given by Aroclor 1232 (the PCB mixture most similar to that burned in waste burn C) or Aroclor 1242. The quantified ECD results are given in Table G.10.

Some of the concentrated sample extracts, e.g., WBB-EPA-FE+PRE, showed no peaks other than solvent. Most of the extracts showed several very small peaks. After quantitation, all but one of the samples were below the level of interest, 0.1 $mg/m^3$, and no further effort was expended. One sample, WBC-ORF-FE, showed a number of peaks, some of which were large. Another sample, WBC-ORF-$H_2O$E, showed a large number of small peaks. Both of these samples were analyzed by GC/MS. The GC/MS analyses of the filter extract indicated one vanishing small hydrocarbon peak, a small phthalate ester peak, and 10 peaks which were various trimethylsilyl compounds (TMS). The GC/MS analyses of the water extract showed extremely small hydrocarbon peaks and 16 peaks that were trimethylsilyl compounds. Because these TMS compounds were most likely the result of some contamination, the peaks appearing in the chromatograms were considered spurious.

TABLE G.10. RESULTS AND DETECTION LIMITS FROM GC/ECD ANALSIS OF THE CONCENTRATED EXTRACTS

| Sample ID | μg/μl as Benzene[d] | μg/μl as Halocarbon[d] | Volume of Sample, ml[a] | Aliquot Factor[b] | Fraction of Sample[c] | Volume of Sample Gas, Std. $m^3$ | Detectable Limits of Concentration in Flue Gas, $mg/m^3$ |
|---|---|---|---|---|---|---|---|
| BLA-EPA-FE+PRE-T3 | ND(<0.002)[e] | - | 75 | 67/20 | 1/4 | 3.76 | ND(<0.05) |
| -IE-T3 | ND(<0.002) | - | 25 | 21/10 | 1/4 | 3.76 | ND(<0.03) |
| -ORF-FE-T3 | ND(<0.002) | - | 50 | 46/10 | 1/4 | 0.32 | ND(<0.3) |
| -H2OE-T3 | ND(<0.002) | - | 25 | 21/10 | 1/4 | 0.32 | ND(<0.3) |
| -PRE+NAOHE-T3 | ND(<0.002) | - | 50 | 42/20 | 1/4 | 0.32 | ND(<0.6) |
| WBB-EPA-FE+PRE | - | ND(<0.002) | 225 | 213/10 | 1/4 | 9.62 | ND(<0.009) |
| -IE | - | ND(<0.002) | 75 | 63/10 | 1/4 | 9.62 | ND(<0.01) |
| -ORF-FE | - | ND(<0.002) | 150 | 138/10 | 1/4 | 0.83 | ND(<0.1) |
| -H2OE | - | ND(<0.002) | 50 | 42/10 | 1/4 | 0.83 | ND(<0.1) |
| -PRE+NAOHE | - | ND(<0.002) | 100 | 92/10 | 1/4 | 0.83 | ND(<0.1) |
| WBC-EPA-FE+PRE | - | ND(<0.002) | 225 | 213/10 | 1/4 | 9.97 | ND(<0.009) |
| -IE | - | ND(<0.002) | 75 | 63/10 | 1/4 | 9.97 | ND(<0.01) |
| -ORF-FE | - | ND(<0.002) | 150 | 138/10 | 1/4 | 0.73 | ND(<0.1) |
| -H2OE | - | ND(<0.002) | 75 | 63/10 | 1/4 | 0.73 | ND(<0.1) |
| -PRE+NAOHE | - | ND(<0.002) | 150 | 138/10 | 1/4 | 0.73 | ND(<0.1) |

[a] Volume of sample received by TRW.

[b] Aliquot Factor: for example 67 ml of the 75 ml BLA-EPA-Fe+PRE sample received was concentrated to 20 ml for analysis.

[c] Fraction of sample. All samples received by TRW were 25% of the total sample.

[d] The instrument was calibrated with benzene or Aroclor 1232. However, the Aroclor peak pattern was not found in any sample chromatogram. High sensitivity GC/MS (3μg/$m^3$ of flue gas) did not detect any chlorinated species in samples WBC-ORF-FE and WBC-ORF-H2OE.

[e] ND = Not detected, values in parentheses indicate the detection limits.

These GC/MS analyses did not detect any chlorinated species in either sample (typical sensitivity of 3 μg/$m^3$ of the flue gas).

2) Aliquots of neat extracts - There was concern that the process of concentrating the sample extracts, as received in pentane and/or hexane, might cause the loss of relatively low boiling halocarbons such as chloroform which might be expected in the samples. Therefore, the retained portions of the as-received extract samples were chromatographed on the Tracor instrument. The column was operated isothermally at 70°C to increase resolution of low boiling compounds. The results are given in Table G.11.

Most of the samples showed no peaks other than solvent. Of those samples showing peaks other than solvent, all quantified below the level of interest (0.1 mg/$m^3$), and no compound identification by GC/MS was performed.

3) Materials desorbed from sorbent tubes - The sorbent traps were desorbed as discussed in Section G.3.1. Portions of the desorbed vapours contained in the sample bulbs were chromatographed isothermally at 70°C with electron capture detection. The samples were qualitatively similar to the sorbent trap blank (unused chromosorb 102) and the baseline B (fuel oil burn) samples. The waste burn B samples each contained a peak which might be $CH_3Cl$: WBB Test 1, 0.0001 mg/$m^3$; and WBB Test 2, 0.0002 mg/$m^3$. The waste burn C samples were essentially the same, qualitatively and quantitatively as the blank and baseline B samples.

G.4.2.2 Inorganic characterization. Inorganic elemental concentrations in the flue gas were determined by analysis of the particulate filters and the aqueous probe rinse and impinger samples. The filters (including the filtered probe rinse insolubles) were all acid digested. Out of these 20 digests (18 test samples and two blanks), three samples were prepared for a trace element survey analysis by combining equal aliquots from each of the three tests of WBB, WBC and BLB using the filter samples from only the EPA sampling train. The EPA train samples were selected on the basis of 1) representing larger sample gas volumes, and 2) having been taken by a method specific for accurate and representative particulate sampling. The results of the survey analysis are shown in Table G.12. The blank

TABLE G.11. RESULTS AND DETECTION LIMITS FROM GC/ECD ANALYSIS OF THE UNCONCENTRATED EXTRACTS

| | ng/µl as Halocarbon[c] | Volume of Sample[a] | Fraction of Sample[b] | Volume of Sample Gas, Std. $m^3$ | Concentration in Flue Gas, $mg/m^3$ |
|---|---|---|---|---|---|
| BLA-EPA-FE+PRE-T3 | ND(<0.0038)[d] | 75 | ¼ | 3.76 | ND(<0.0003) |
| -IE-T3 | ND(<0.0038) | 25 | ¼ | 3.76 | ND(<0.0001) |
| -ORF-FE-T3 | ND(<0.0038) | 50 | ¼ | 0.32 | ND(<0.002) |
| -$H_2$OE-T3 | 0.0051 | 25 | ¼ | 0.32 | 0.0016 |
| -PRE-NAOHE-T3 | ND(<0.0038) | 50 | ¼ | 0.32 | ND(<0.0024) |
| WBB-EPA-FE+PRE | ND(<0.0038) | 225 | ¼ | 9.62 | ND(<0.0004) |
| -IE | 0.40 | 75 | ¼ | 9.62 | 0.012 |
| -ORF-FE | ND(<0.0038) | 150 | ¼ | 0.83 | ND(<0.003) |
| -$H_2$OE | ND(<0.0038) | 50 | ¼ | 0.83 | ND(<0.0009) |
| -PRE+NAOHE | ND(<0.0038) | 100 | ¼ | 0.83 | ND(<0.0018) |
| WBC-EPA-FE+PRE | ND(<0.0038) | 225 | ¼ | 9.97 | ND(<0.0003) |
| -IE | 0.10 | 75 | ¼ | 9.97 | 0.0030 |
| -ORF-FE | ND(<0.0038) | 150 | ¼ | 0.73 | ND(<0.0031) |
| -$H_2$OE | 0.15 | 75 | ¼ | 0.73 | 0.061 |
| -PRE+NAOHE | ND(<0.0038) | 150 | ¼ | 0.73 | ND(<0.0031) |

[a] Volume of sample received by TRW.

[b] Fraction of sample. All samples received by TRW were 25% of the total sample.

[c] The instrument was calibrated with Aroclor 1232. However, the Aroclor peak pattern was not found in any sample chromatogram. High sensitivity GC/MS (3 µg/$m^3$ of flue gas) did not detect any chlorinated species in samples WBC-ORF-FE and WBC-ORF-H2OE.

[d] ND = Not detected. Values in parentheses indicate detection limits.

TABLE G.12. TRACE METAL SEMI-QUANTITATIVE[a] SURVEY OF FILTER DIGESTS BY ICPOES

| Element | Average Concentration[b] (mg/m$^3$) | | |
|---|---|---|---|
| | WBB | WBC | BLB |
| Al | 0.078 | 0.51 | 0.26 |
| Ba | 0.011 | 0.014 | 0.012 |
| B | 0.018 | 0.084 | 0.038 |
| Ca | 2.2 | 11. | 6.5 |
| Cd | 0.0006 | 0.002 | 0.001 |
| Cr | 0.003 | 0.006 | 0.004 |
| Co | ND[c] | 0.001 | ND[c] |
| Cu | 0.003 | 0.007 | 0.003 |
| Fe | 0.18 | 1.1 | 0.73 |
| Pb | 0.047 | 0.12 | 0.044 |
| Mg | 0.076 | 0.38 | 0.21 |
| Mn | 0.003 | 0.018 | 0.013 |
| Ni | 0.003 | 0.006 | 0.002 |
| P | 0.014 | 0.055 | 0.044 |
| K | 14. | 32. | 6.7 |
| Si | 0.082 | 0.051 | 0.093 |
| Ag | 0.0003 | 0.003 | 0.0004 |
| Na | 1.8 | 5.5 | 2.4 |
| Sr | 0.004 | 0.013 | 0.0008 |
| Ti | 0.002 | 0.008 | 0.004 |
| V | 0.0006 | 0.002 | 0.001 |
| Zn | 0.014 | 0.042 | 0.027 |

[a] Accuracy estimated to be a factor of ±2 or better.

[b] Calculated based on average sample gas volumes of:

WBB - 3.2 m$^3$
WBC - 3.3 m$^3$
BLB - 3.4 m$^3$

Not corrected for filter contribution

[c] Not detected (<0.0003 ppm)

(an acid digest of unused filters) sample was not surveyed, so the values reported in this table are uncorrected for the filter background.

Of the 32 elements that can be determined by the ICPOES analysis, ten were not detected in the filter digest samples. These ten elements with their lower detection limits are listed in Table G.13, along with a calculation of the average detectable limit for each of these elements in the flue gas.

TABLE G.13. LIMITS OF DETECTION FOR UNDETECTED ELEMENTS BY ICPOES

| Element | ICPOES Detection Limit (ppb) | Average Detectable[a] Limit in Flue Gas (mg/m$^3$) |
|---|---|---|
| Au | 5 | 0.00008 |
| As | 40 | 0.0006 |
| Be | 1 | 0.00002 |
| Eu | 15 | 0.0002 |
| Mo | 11 | 0.0002 |
| Se | 60 | 0.0009 |
| Te | 65 | 0.0010 |
| Sn | 50 | 0.0008 |
| W | 90 | 0.0014 |
| U | 80 | 0.0012 |

[a] Based on an average sample gas volume of 3.3 cubic meters.

The results of this survey indicated only one element, lead, was present at potentially toxic levels in the stack. While not a problem with the stack configuration in the present study, the concentration and the effect of thermal dispersion should be considered when extrapolating these results to other kilns. To be sure of an accurate measurement of the levels of lead and certain other toxic metals which the waste analysis indicated might be present at levels of interest, a quantitative determination by AAS was performed on five elements. The results from this analysis are presented in Table G.14.

The AAS results were corrected for background levels as determined by analysis of the filter blank sample. It should be noted that background contributions were not only from trace contaminants in the filter materials but also in some cases from matrix effects in the mixed acid solutions.

AAS was also used to analyze for selected elements in the aqueous probe rinse and impinger samples. Table G.15 lists the results from these analyses and shows that, in general, nothing significant was found. No background or blank solutions were available so the BLB results should be used to correct for background effects. The results for these aqueous samples were left in ppm because the total sample volumes were unknown.

TABLE G.14. CONCENTRATION OF TRACE METALS IN EFFLUENT GAS PARTICULATE MATTER BY AAS

| Waste Burn | Train | Test | Concentration of Element (mg/m$^3$) | | | | |
|---|---|---|---|---|---|---|---|
| | | | Ba | Cd | Co | Cr | Pb |
| WBB | EPA | 1 | ≤0.008[a] | ≤0.001 | ≤0.002 | ≤0.009 | 0.028 |
| | | 2 | ≤0.008 | ≤0.001 | ≤0.001 | ≤0.002 | 0.012 |
| | | 3 | ≤0.008 | 0.001 | ≤0.002 | ≤0.004 | 0.079 |
| WBC | EPA | 1 | 0.013 | 0.001 | ≤0.002 | ≤0.008 | 0.096 |
| | | 2 | ≤0.008 | 0.002 | ≤0.002 | ≤0.008 | 0.103 |
| | | 3 | 0.027 | 0.003 | ≤0.002 | 0.003 | 0.153 |
| BLB | EPA | 1 | ≤0.007 | 0.001 | ≤0.002 | 0.001 | 0.040 |
| | | 2 | ≤0.008 | 0.002 | ≤0.003 | ≤0.007 | 0.062 |
| | | 3 | ≤0.008 | 0.001 | ≤0.002 | ≤0.002 | 0.015 |

[a] "≤", a less than or equal to sign, indicates those elements which were detected but not significantly above background levels.

TABLE G.15. CONCENTRATION OF TRACE METALS IN AQUEOUS SAMPLES BY AAS

| Train/Component | Waste Burn vs. Baseline | Concentration of Element (ppm) | | | |
|---|---|---|---|---|---|
| | | Pb | Cr | Cd | Co |
| EPA-Probe Rinse | WBB | ND | 1.9 | ND | 10.2 |
| | WBC | ND | 0.03 | 0.01 | ND |
| | BLB | ND | ND | ND | ND |
| Impingers | WBB | ND | ND | ND | 0.05 |
| | WBC | ND | 0.02 | ND | ND |
| | BLB | ND | ND | ND | ND |

Analysis of the filter acid digest, probe rinse, and impinger samples from the ORF train by AAS confirmed the presence of those elements found in the EPA train samples. However, since the ORF train was not operated with the intent of collecting an accurate particulate sample (i.e., isokinetic, traverses, etc.) the AAS results for this train were not calculated out to concentrations in the flue gas.

### G.4.3 Solid residues and effluents from the SLC kiln process

Of the four types of solid samples collected during the test program:

- clinker product;
- clinker fines;
- electrostatic precipitator discard dust; and
- cement mixes,

analyses were performed only on the clinker product and discard dusts for the following reasons. The clinker fines were recovered from air blown through the clinker product and were then returned to the clinker storage. The cement mixes were simply clinker product with gypsum added. Thus, neither of these materials represented unique samples. The following paragraphs describe the results of analyses performed on the clinker products (CP) and discard dust (DD) samples. If significant amounts of toxic materials were found in the analyzed samples, further tests on the remaining samples would have been conducted. However, this did not prove to be necessary.

G.4.3.1. Organic constituents. Portions of the clinker product and discard dust samples were extracted with pentane using a Soxhlet extractor and preextracted paper thimbles. A blank sample was prepared by running a pentane extraction on an empty, precleaned thimble. In addition, a doped control sample consisting of ~30 grams of clinker, to which 0.9 mg of a known PCB mixture had been added, was also extracted for analysis. This doped sample represented a PCB concentration ~30 ppm in the clinker product. These samples were all analyzed both qualitatively and quantitatively by the same techniques described in Section G.4.2.1.

Qualitative data. Aliquots of the pentane extracts were evaporated and the residue was weighed and scanned by both IR and LRMS. These results

TABLE G.16. RESULTS OF ORGANIC SURVEY ANALYSIS ON CLINKER PRODUCT AND DISPOSABLE DUST SAMPLES

| Sample Identification | Weight of Extracted Sample (g) | Weight of Residue in Extract (mg) | Qualitative Nature of Residue |
|---|---|---|---|
| BLB-CP | 30.270 | <1.16* | Hydrocarbon oils, phthalate esters, traces of fatty acids and silicones* |
| BLB-DD | 24.185 | 1.31 | |
| WBB-CP | 29.445 | 1.30 | |
| WBB-DD | 18.948 | 1.16 | |
| WBC-CP | 21.816 | <1.16* | |
| WBC-DD | 33.112 | <1.16* | |
| PCB Doped Control | 29.998 | <1.16* | All of the above compounds plus polychlorinated biphenyls |

*The residue obtained from the blank thimble and pentane sample was 1.16 mg. Sample values varied with some being less than 1.16 mg due to the variability of the background. Over this range, the differences in residue weights are not significant.

are summarized in Table G.16. In most cases, the amount of weighable residue found in the extracts did not exceed that found in the blank. The materials identified by IR and LRMS are indicative of the low level contamination by greases, oils, soaps, etc., that often accompanies trace organic analysis. Hydrocarbon oils, phthalate esters, fatty acids, and silicone compounds were found in all the extract residues including the blank. No indication of the chlorinated species was found in any of the test samples.

Polychlorinated biphenyls were clearly detected in the PCB doped control sample. The LRMS spectrum contained peaks at 220, 222, 290, 292, and 294 AMU. The PCB's present at 30 ppm in the doped clinker were easily found and it is certain that much lower levels could have been detected. It is estimated that the mass spectrometer can detect the strongest peaks from a specifically searched for compound when present at the 10 ng level in a 1 milligram organic residue from the clinker. This results in a lower limit of detection by this qualitative survey technique of about 1 ppb in the clinker or dust. The IR survey data was not useful in detecting PCB's at this level.

Quantitative data. The clinker and dust extracts were analyzed by GC with both FID and ECD detection. The results are given in Tables G.17 and G.18, respectively. Using the FID, no peaks other than solvent were found, and the results are expressed as minimum detectable quantities. Three of the samples showed no peaks other than solvent when analyzed with the ECD. The three samples which had peaks other than solvent using the ECD were quantitated at well below the level of interest.

To ascertain the recovery of PCB's from the clinker and dust samples, a 30 gram sample of clinker was doped with 0.9 mg of Aroclor 1232, extracted and concentrated in the same fashion as the clinker and dust samples. The ECD chromatogram of this artificial sample matched the pattern of a neat sample of Aroclor 1232, and the recovery of PCB's from the doped sample was calculated as 25%. This recovery factor has been applied to the clinker and dust samples in Tables G.17 and G.18. (The recovery factor is the reason why the values for the samples in Table G.17 exceed several ppm. If the minimum detectable quantity using the FID is 0.002 μg/μl, then after applying the recovery factor, the concentration in the sample cannot exceed 0.008 μg/μl. For a 10 ml extract volume and a 30 g clinker sample, the composition is thus <2.7 μg/g.)

G.4.3.2 Inorganic characterization. The CP and DD samples were also examined for trace metal content by spark source mass spectrometry (SSMS). The major constituents of both types of material were determined to be aluminum, calcium, iron, magnesium, sodium, sulphur, and silicon. Other trace inorganic elements which were detected down to a 1 ppm concentration are listed in Table G.19. It should be remembered that SSMS data are semi-quantitative. The values reported should be considered as being accurate within 500% of the true value.

The trace metal character of the clinkers and dusts did not change significantly from one waste burn to the other. The relatively low feed rate of the wastes, compared to that of the precursor material and the primary fuel, appeared to make any contribution of trace metals from the wastes negligible.

### TABLE G.17. RESULTS AND DETECTION LIMITS FROM GC/FID ANALYSIS

| Sample ID | μg/μl as Halocarbon[a] | Volume of Sample (ml) | μg/g of Sample Material |
|---|---|---|---|
| BLB-CP | ND(<0.002)[b] | 10 | ND(<3.0) |
| WBB-CP | ND(<0.002) | 10 | ND(<3.3) |
| WBC-CP | ND(<0.002) | 10 | ND(<4.5) |
| BLB-DD | ND(<0.002) | 10 | ND(<3.9) |
| WBB-DD | ND(<0.002) | 10 | ND(<5.1) |
| WBC-DD | ND(<0.002) | 10 | ND(<2.9) |

[a] The instrument was calibrated with Aroclor 1232. However, the Aroclor peak pattern was not found in any sample chromatogram.

[b] ND = Not detected. Values in parentheses indicate detection limits.

### TABLE G.18. RESULTS AND DETECTION LIMITS FROM GC/ECD ANALYSIS

| Sample ID | ng/μl as Halocarbon[a] | Volume of Sample (ml) | μg/g of Sample Material |
|---|---|---|---|
| BLB-CP | 0.059 | 10 | 0.02[c] |
| WBB-CP | 0.11 | 10 | 0.04[c] |
| WBC-CP | ND(<0.004)[b] | 10 | ND(<0.002) |
| BLB-DD | ND(<0.004) | 10 | ND(<0.002) |
| WBB-DD | ND(<0.004) | 10 | ND(<0.002) |
| WBC-DD | 0.060 | 10 | 0.02[c] |
| CP+PCB | 22.4 | 10 | 7.5 |

[a] The instrument was calibrated with Aroclor 1232. However, the Aroclor peak pattern was not found in any sample chromatogram.

[b] ND = Not detected. Values in parentheses indicate detection limits.

[c] No chlorinated species were detected in the qualitative survey of these samples by LRMS.

### TABLE G.19. SELECTED TRACE METALS IN SLC CLINKER PRODUCT AND DISCARD DUST SAMPLES BY SSMS

| | Concentration (ppm)[a] | | | | | |
|---|---|---|---|---|---|---|
| | WBB | | WBC | | BLB | |
| Element | CP | DD | CP | DD | CP | DD |
| As | <1.5 | 3 | <1.5 | 3 | <2.9 | 1 |
| B | 30 | 30 | 30 | 10 | 30 | 30 |
| Ba | 70 | 70 | 300 | 100 | 70 | 30 |
| Be | ND[b] | ND | 1 | ND | 7 | ND |
| Ce | 10 | 30 | 70 | 30 | 10 | 10 |
| Co | ND | ND | ND | 3 | 1 | ND |
| Cr | 7 | 10 | 30 | 10 | 30 | 10 |
| Cu | 1 | 10 | 3 | 7 | 7 | 3 |
| Cs | ND | 10 | ND | 30 | ND | 10 |
| Dy | 1 | ND | 3 | 1 | 1 | ND |
| Ga | 1 | 1 | 3 | 1 | 3 | 10 |
| Ge | ND | ND | ND | ND | 1 | 3 |
| La | 7 | 7 | 30 | 10 | 10 | 7 |
| Li | ND | ∼1000 | 30 | 100 | 100 | 100 |
| Mn | 100 | 100 | 300 | 300 | 300 | 100 |
| Mo | 1 | 1 | 1 | 1 | 3 | 1 |
| Nb | 3 | 3 | 7 | 3 | 3 | 3 |
| Nd | 10 | 10 | 10 | 10 | 10 | 7 |
| Ni | 7 | 3 | 7 | 7 | 10 | 3 |
| Pb | ND | 70 | 3 | 100 | ND | 30 |
| Pr | 3 | 3 | 10 | 3 | 3 | 1 |
| Rb | 7 | 100 | 10 | 300 | 10 | 70 |
| Sc | ND | 1 | ND | ND | 7 | 3 |
| Se | ND | 10 | ND | 3 | 1 | 1 |
| Sm | ND | ND | 1 | 1 | 1 | ND |
| Sr | 700 | 300 | 700 | 700 | 700 | 100 |
| Th | 1 | 7 | 7 | 7 | 3 | 1 |
| Ti | 700 | 700 | 700 | 700 | 700 | 700 |
| U | ND | 1 | 3 | 3 | 1 | ND |
| V | 30 | 30 | 30 | 30 | 70 | 30 |
| Y | 3 | 3 | 7 | 10 | 3 | 3 |
| Zn | 30 | 30 | 70 | 100 | 30 | 30 |
| Zr | 30 | 30 | 100 | 70 | 70 | 10 |

[a] SSMS data generally ranges within 500% accuracy.

[b] ND - Not Detected (<1 ppm).

## REFERENCES

G.1 Communication, Gordon Thomas, Ontario Research Foundation to Arnold Grant, TRW Systems, 7 April, 1976

# APPENDIX H

## DEVELOPMENT, CONSTRUCTION AND EVALUATION OF A COLLECTION SYSTEM FOR LOW MOLECULAR WEIGHT HALOCARBONS

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# APPENDIX H

## DEVELOPMENT, CONSTRUCTION AND EVALUATION OF A COLLECTION SYSTEM FOR LOW MOLECULAR WEIGHT HALOCARBONS

### H.1 Summary

Numerous experiments have been performed to determine the effectiveness of absorbents and adsorbents to remove and retain low molecular weight halocarbons from a flowing gas stream. Initial studies using a particulate sampling train, requiring a high gas flow rate of at least 0.5 cfm, indicated that neither absorbents nor adsorbents would efficiently collect compounds such as chloroform ($CHCl_3$) present in the gas stream at low concentrations of a few parts per billion. An inert adsorbent, e.g. Chromosorb 102, was found, however, to efficiently remove and retain $CHCl_3$ at much lower gas flow rates of 0.2 - 1.0 litres/minute. A collection system for low molecular weight halocarbons was constructed and evaluated at low flow rates over sampling periods of up to four hours duration. Results obtained from several tests indicated that the system had a collection efficiency of better than 90% over the longest time period. Desorption of adsorbed halocarbons was readily achieved by thermal treatment of the adsorbent.

### H.2 Introduction

Late in 1975, an experimental program to burn waste chlorinated organic compounds in a rotary cement kiln was carried out at the St. Lawrence Cement Company (SLC) plant in Mississauga, Ontario. The program, sponsored by Environment Canada, was designed to obtain information on

- the use of waste chlorinated hydrocarbons as a supplemental fuel to the kiln;
- the reduction of alkali concentration of the clinker by the chlorine contained in the waste materials added; and,
- the effect of emissions from the kiln on air quality.

In order to collect the required information, process and emission samples were collected during periods when different composite wastes were burned in the kiln. The emission samples were analyzed for trace chlorinated organic compounds.

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During preliminary discussions between members of the Ontario Ministry of the Environment (MOE), the Ontario Research Foundation (ORF) and SLC prior to initiating the study, some concern was expressed about the sampling methodology for trace chlorinated organic compounds. Since a major program requirement was to obtain the particulate emission rate during each burn, it was hoped that the EPA Method 5 sampling train, used to collect particulate material, could also be used for the collection of chlorinated organic compounds. However, it was not known whether absorbents or adsorbents were more efficient for collection of the organic compounds, or whether either collection medium would be efficient at the high gas flow rates required for particulate sampling.

MOE, therefore, requested that ORF complete a laboratory investigation to evaluate suggested procedures, and to develop an optimum method for the sampling and collection of trace chlorinated organic compounds which might be present in the kiln emissions. This report describes the test program carried out in the laboratory and presents the data obtained using specific chlorinated compounds as representative pollutants.

## H.3 Background Information

Previous studies involving the incineration of chlorinated organic compounds [H.1] have indicated that, if complete combustion to $CO_2$, $H_2O$ and $Cl_2$ or HCl is not realized, then trace amounts of volatile compounds such as $CCl_4$, $CHCl_3$ and $CH_2Cl_2$ may be present in the combustion gases. (Though it was unlikely that any HCl or $Cl_2$ produced would pass through a cement kiln without reacting to form alkali chlorides, it was necessary to consider these gases as possible pollutants for analysis also.)

The EPA Method 5 train for particulate sampling is also used to collect organic compounds in the impingers by condensation and scrubbing. The efficiency of collection for a particular substance is dependent on gas flow rate and volatility of the organic compound. For compounds more volatile than water, the collection efficiency is probably close to zero. To collect these volatile compounds, specific organic solvents have been used in the impingers, replacing the water normally present. There is, however, little data available on the collection efficiencies obtained.

In recent years, organic compounds in the ambient air have been collected using inert adsorbents [H.2]. These materials have tended to replace activated carbon for most applications since they are unaffected by water vapour, and recovery of adsorbed species is considered, in general, to be easier and more efficient. Recovery of adsorbed species may be accomplished either by thermal desorption or solvent extraction. An application of this technique has been to collect polycyclic organic compounds from combustion effluents [H.3].

Bearing in mind that, in the study to be carried out at SLC only trace amounts of more volatile organic compounds were expected to be in the kiln emissions, it was decided to evaluate both adsorbents and adsorbents in an EPA Method 5 sampling train for collection, retention and subsequent recovery of compounds such as $CHCl_3$ and $CH_2Cl_2$. If a collection method proved to be effective for capture of these compounds, then it would almost certainly be effective for the collection of higher molecular weight species, such as those chlorinated compounds present in the waste feed material.

## H.4 Test Methodology

The normal gas flow rate through a particulate sampling train to maintain isokinetic sampling for most sources is 0.5 to 1.0 cfm. A flow rate of 0.5 to 0.7 cfm was, therefore, chosen for initial experiments using the EPA Method 5 train, which was illustrated in schematic form as Figure A.5 in Appendix A.

### H.4.1 Retention and collection studies

H.4.1.1 Absorbents. Initially, tests were conducted to find a suitable high boiling solvent for use in an impinger system, in order to trap low molecular weight organochlorine compounds, e.g. $CHCl_3$, $CCl_4$, DCE and TCE.

The following solvents were tested for their suitability as an impinger solution for use in an EPA stack sampling train:

- reagent grade toluene;
- reagent grade xylene; and,
- reagent grade decane.

All solvents were redistilled prior to use in order to remove or limit to usable level interfering peaks in the GC-EC chromatographic profiles which tended to obscure measurement of the components of interest.

Tests were made to see if trace quantities of volatile chlorinated compounds could be retained in a solvent such as toluene with a high gas flow rate passing through the train for a period of four hours, a time anticipated for tests at SLC. A sampling train was, therefore, assembled in the laboratory with probe and oven temperature set above 250°F to warm incoming gas.

Toluene (100 ml) containing known amounts of 1,2-dichloroethane (EDC) and 1,1,2-trichloroethane (TCE) (main constituents of the first waste feed in the waste chloride study at SLC) was placed in impinger A (see Figure A.5). 100 ml of pure toluene was placed in impinger B, impinger C was empty and impinger D contained silica gel. Air was pulled through the sampling train after cooling the impingers to ice-water temperature, at a flow rate of 0.5 cfm. After running for four hours, the contents of each impinger were noted and analyses made for EDC and TCE. At specific times during each test, the parameters normally recorded during a source sampling test, such as impinger inlet and outlet temperatures and orifice Δp, were recorded. At the conclusion of each test, the total volume of gas sampled was determined.

This type of experiment was repeated, with 100 ml of water in impinger A, 100 ml of toluene containing EDC and TCE in impinger B, impinger C empty and impinger D containing silica gel. Both experiments were then repeated using xylene and decane as absorbents. Additional experiments were made using decane with known quantities of $CCl_4$, $CHCl_3$ and $CHCl_2$ in the standard impinger solution.

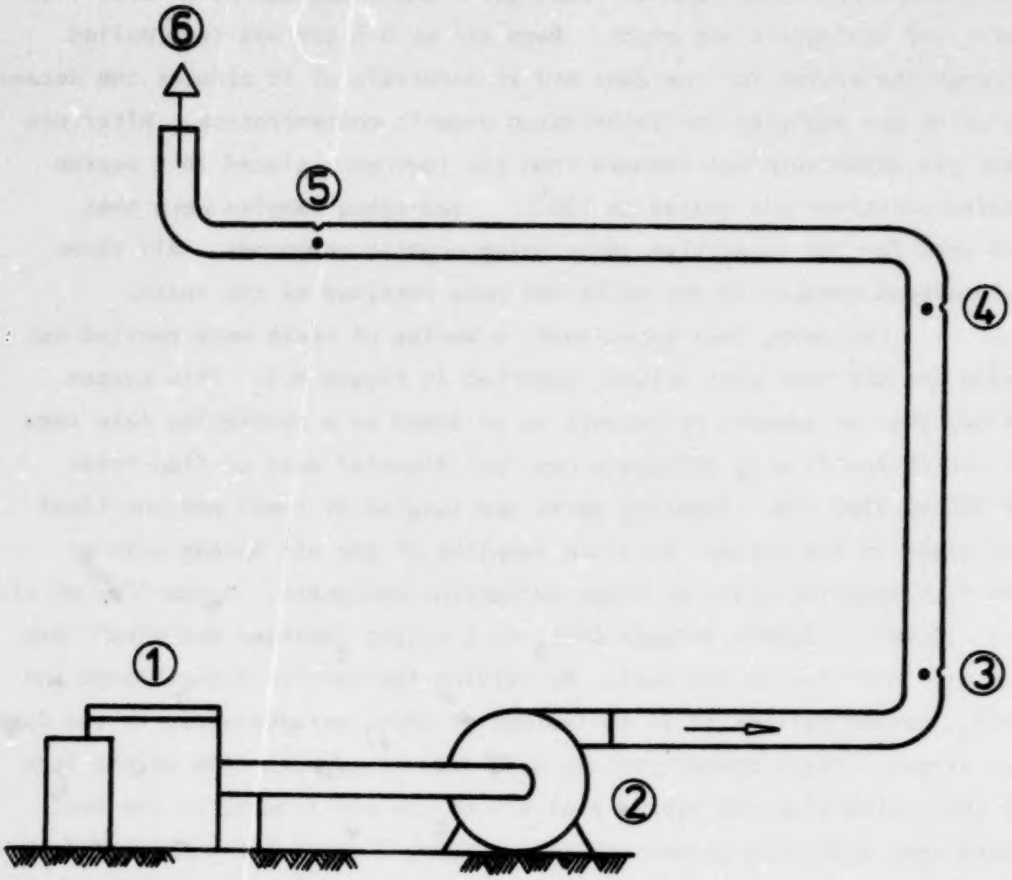
H.4.1.2 Adsorbents. Though a large number of adsorbents are capable of adsorbing a wide variety of organic compounds, Chromosorb 102 was used for the tests described below because it was readily available, and could be purchased without delay from various companies supplying chromatographic materials.

In order to determine fairly rapidly if Chromosorb 102 would adsorb volatile chlorinated compounds, the following experiment was performed. 100 ml of decane containing known quantities of $CCl_4$, $CHCl_3$ and TCE was placed in impinger B of the sampling train, and 25 gm of

Chromosorb 102 in impinger D. Impinger A contained 200 ml of distilled water and impinger C was empty. Room air at 0.5 cfm was then pulled through the system for one hour and at intervals of 10 minutes the decane solution was analyzed for chlorinated organic concentration. After one hour the Chromosorb was removed from the impinger, placed in a septum sealed container and heated to 100°C. Head-space samples were then analyzed for the respective chlorinated organic compounds. All three halocarbons present in the spike had been retained by the resin.

Following this experiment, a series of tests were carried out using the ORF test duct system, depicted in Figure H.1. This system allows dust or gaseous pollutants to be added at a controlled rate into an air stream flowing through a one-foot diameter duct at flow rates of 500 to 2500 cfm. Sampling ports are located at ideal and non-ideal positions in the system, to allow sampling of the air stream with an EPA type sampling train or other collection equipment. A low flow of air was allowed to bubble through $CHCl_3$ in a midget impinger and bleed into the main air flow in the duct. By varying the carrier flow through the $CHCl_3$, concentrations of 10 to 140 ppb of $CHCl_3$ were obtained in the duct air stream. These concentrations were determined both from weight loss of $CHCl_3$ with time and direct analysis of the air flowing in the duct. Tests were made with Chromosorb in impingers C and D but considerable carry over of the adsorbent occurred at flow rates of 0.5 - 0.7 cfm. This was minimized in further tests by placing a fine mesh screen on top of the Chromosorb layer in the impinger. At a $CHCl_3$ concentration of 13 ppb, breakthrough of this pollutant with 25 gm of Chromosorb in the third impinger occurred within 30 minutes.

It was recognised that high volume flow rates through the adsorbent caused not only contaminant problems with the material in the sampling train but saturated the bed fairly rapidly. This latter occurrence was proved by repeating the experiment with the Chromosorb packed tightly in a collector. A final series of tests were, therefore, completed, evaluating both Chromosorb and activated carbon in tube collectors at much lower air flow rates of 1-2 litres/minute. The $CHCl_3$ concentration in the air stream was analyzed before and after the collector at selected time intervals over a period of four hours. For both adsorbents collection of $CHCl_3$ was more than 90% efficient for the duration of each test. Since



1 DUST FEEDER
2 BLOWER
3 SAMPLING PORTS NON IDEAL LOCATION
4 SAMPLING PORTS IDEAL LOCATION
5 SAMPLING PORTS
6 TO ATMOSPHERE

FIGURE H.1 TEST DUCT SCHEMATIC

desorption of adsorbed species from Chromosorb was readily accomplished thermally and since, unlike activated carbon, the adsorption characteristics of Chromosorb are unaffected by moisture in the gas stream, Chromosorb 102 was selected as a suitable adsorbent for the SLC waste chloride program.

### H.5 Collection System Evaluation

This section outlines the experimental protocol undertaken to verify the performance of Chromosorb 102 as a collection media for the concentration and analysis (by adsorption/desorption) of low molecular weight chlorinated hydrocarbons from an air stream under conditions relevant to field sampling. The concentration and analysis procedure is essentially an extension of the method used to concentrate organohalogen compounds present in potable water [H.4].

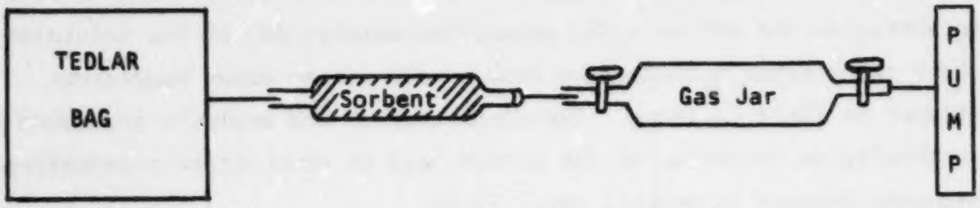
Adsorptive capacity values were determined. Adsorptive capacity is defined as the amount of solute vapour retained by a given weight of sorbent. In this study only low levels of chlorinated hydrocarbons (1 - 10 ppb) were examined since anticipated levels of organohalides in the sampling streams were expected to be low (i.e. ng/m$^3$).

The sampling cartridges consisted of glass tubes (11 mm i.d. x various lengths) containing various depths of sorbent bed supported by plugs of silanized glass wool. The tubes were conditioned by heating to 200$^\circ$C and passing a stream of $N_2$ through them (40 ml/min) for four hours.

Known concentrations of air-solute vapour mixtures were prepared. The solutes examined were $CHCl_3$, $CCl_4$ and dichloroethane (DCE). The solutes were examined both individually and as mixtures. The air-solute vapour mixtures were prepared as follows.

Microlitre quantities of organic compounds were injected into gas jars of known volume. The gas jar was heated to ~ 50$^\circ$C and, after cooling, aliquots were removed and added to Tedlar bags. The bags initially were evacuated and then half filled with air, at which stage the aliquot from the gas jar was injected into the bag. The bag was finally filled to the desired capacity (6, 20 and 40 litres).

A schematic diagram of the component parts of the test assembly is shown below.



The various parts of the assembly were connected to each other by means of Teflon tubing. Differing air-solute mixture concentrations of $CHCl_3$ were used to determine the adsorptive capacity of the Chromosorb 102. The $CHCl_3$ concentrations used were 5 ppb and 10 ppb. A flow rate of 250 ml/min was maintained throughout the run. For these conditions the collection efficiency of Chromosorb 102 for $CHCl_3$ was 100 percent. At various time intervals the pump was stopped and the gas jar disconnected. Aliquots (1 ml) were removed from the gas jar and analyzed for $CHCl_3$ by gas chromatography (GC). The first detection of $CHCl_3$ in the gas jar was taken as the stage in the test for the determination of breakthrough volume, i.e. the volume of air necessary to purge the adsorbed vapour through the cartridge.

From the breakthrough volume of the air-solute mixture of known concentration and the weight of sorbent in the cartridge it was possible to calculate the adsorptive capacity of Chromosorb 102 for $CHCl_3$ under the given experimental conditions.

From the data determined with respect to the adsorptive capacity of Chromosorb 102 for $CHCl_3$ and the knowledge that a four hour sampling period at a flow rate of 250 ml/min would be required in the field tests, sampling cartridges of the following dimensions were constructed: 11 mm i.d. x 11.5 cm long containing 6 g of Chromosorb 102. These cartridges were used to determine desorption efficiency data.

$$\text{Desorption efficiency} = \frac{\text{quantity } CHCl_3 \text{ from Chromosorb 102}}{\begin{matrix}CHCl_3 \text{ concentration} \\ \text{in air sampled}\end{matrix} \times \begin{matrix}\text{Volume of air} \\ \text{sampled}\end{matrix}}$$

The same test assembly as described previously was used to collect $CHCl_3$ on the cartridge. The adsorbed $CHCl_3$ was thermally desorbed into an evacuated gas jar. The adsorbent tube and the gas jar were connected by Teflon tubing. The tube was heated to a fixed temperature by wrapping with heating tape controlled by a variable transformer (170°C). After reaching maximum temperature, the stopcock of the gas jar between the jar and the tube was opened. Heating of the sample tube was continued for a further 15 minutes, after which time the stopcock of the gas jar was closed, the gas jar removed from the sample tube, taken outside the laboratory and allowed to fill up with the cleanest possible air. The contents of the gas jar were then subjected to GC analysis. Aliquots (1 ml) were removed from the gas jar using an air-tight syringe and injected into a gas chromatograph.

Gas chromatography was conducted on a Varian 1200 series chromatograph equipped with an electron capture detector. The GC parameters used are shown below.

| | |
|---|---|
| Column | - 2 m x 2 mm SS containing Chromosorb 102 (80/100 mesh) |
| Column temperature | - 180°C |
| Injector temperature | - 215°C |
| Detector temperature | - 215°C |
| Detector | - EC |
| Flow rate | - $N_2$ ~ 31 ml/min |
| Range and attenuation | - as required |
| Chart speed | - as required |

The concentration of solutes present in the gas jars following desorption was determined by measuring peak areas of the vapours and comparing them with those of prepared standards. The initial concentration

In the Tedlar bag was known, and, from the volume of air drawn through the cartridge, the actual concentration contacting the cartridge was calculated. The desorption efficiency was then calculated.

## H.6 Results and Discussion

Experiments using toluene and xylene as absorbents showed that a considerable loss of both solvent and chlorinated organic compounds occurred after a four hour test. The solvent was found in all impingers following the one in which the standard solution was placed. Estimated solvent losses were 40-60%. Losses of $CCl_4$, $CHCl_2$ and TCE ranged from 50 to 90%. With decane as the adsorbent, the solvent loss was less than 10%. However, the loss of chlorinated compounds was 60 to 100%. Due to time restraints and the obvious problem of solvent or pollutant loss at the high gas flow rate, this method of collection using absorbents was rejected.

As discussed in Section H.4.1.2, retention of volatile halocarbons by the adsorbent at high gas volume flow rates was poor and the breakthrough rapid. The results for the collection system finally selected (Section H.5) are summarized below.

Adsorptive Capacity

| Component | µl/g (sorbent) |
|---|---|
| $CHCl_3$ | 0.1 |

Desorption Efficiency

| Tedlar bag concentration of $CHCl_3$ | Desorption Efficiency % |
|---|---|
| 1.25 ppb | 90 |
| | 96 |
| | 104 |
| 5.0 ppb | 92 |
| | 110 |
| 10.0 ppb | 94 |
| | 102 |

(The higher concentration samples required a second thermal desorption in order to remove all the solute from the sorbent. However, the first desorption was always better than 75%.)

Two additional experiments were performed. They were:

a) An air-solute mixture of $CCl_4$ and DCE (5.00 ppb level; 40 ℓ Tedlar bag) was run through the system using a back-up gas jar in order to test whether these solutes were retained by the Chromosorb 102. Regular checks of the gas jar using GC to analyze for the presence of $CCl_4$ and/or DCE failed to show any trace. Thermal desorption of the tube followed by GC analysis gave good recoveries for $CCl_4$ and DCE (>90%).

b) An air-solute mixture of $CHCl_3$, $CCl_4$ and DCE (2.5 ppb level; 40 ℓ Tedlar bag) was prepared. This mixture was drawn through the test system which contained two additional traps prior to the Chromosorb 102 cartridge. One trap contained water (50 ml) and the other 5% NaOH solution (80 ml). These traps were included in the ORF train in order to remove residual $Cl_2$ and/or HCl. Thermal desorption of the tube contents gave good recoveries of the solutes (>90%).

## H.7 Conclusions

The laboratory study undertaken showed that low molecular weight halocarbons cannot be efficiently collected by absorbents or adsorbents from a gas stream at high flow rates (∿ 0.5 cfm).

There are numerous literature references to the technique for collecting trace quantities of component vapours by drawing air through cartridges containing sorbent media such as polymer beads, activated carbons or stationary liquid phases chemically bonded to solid supports [H.5].

This report has demonstrated such a procedure for the collection of low molecular weight chlorinated hydrocarbons on Chromosorb 102. It has been shown to give quantitative collection together with quantitative recovery of the trapped species using a thermal desorption technique.

The sampling tube technique appears to give better results for sampling traces of low molecular weight organochlorine pollutants in air than impinger methods.

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# APPENDIX I

## GC/MS/COMPUTER DETERMINATION OF CHLORINATED HYDROCARBONS AND PCB'S

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Air Pollution Control Directorate
Environmental Protection Service
Environment Canada

Submitted by
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## APPENDIX I

## GC/MS/COMPUTER DETERMINATION OF CHLORINATED HYDROCARBONS AND PCB's

In February 1970, 30 extracted samples were received from Dr. G. Thomas of the Ontario Research Foundation. These samples were taken from the burning of chlorinated hydrocarbon wastes in a cement kiln. Requests were made to determine the nature and quantity of any heavy chlorinated hydrocarbons, in particular PCB's, present in the samples.

Experiments were completed and the procedures are briefly described as follows:

Material: All apparatus and reagents used in the experiment were examined by gas chromatograph-flame ionization detector (GC-FID) analysis of a pure hexane extract to ensure freedom from organochlorine residue contamination. The chlorinated isomers (PCB's) and Aroclor mixtures were obtained from Analabs, North Haven, Conn., U.S.A.

GC-FID: A Perkin-Elmer 990 model GC-FID with a datasystem PGP-1 was used. The procedures for standard calibrations were given in a previous paper (to be published as a chapter in the book "Advances in Dynamic Mass Spectrometry" 1976). Chromatograph operating parameters were as follows:

| | |
|---|---|
| Column 12' x 1/8" O.D. | stainless steel |
| Column packing | 6% Apiezon L on chromosorb W 80/100 mesh |
| Column temperature | Initial 100°C programmed at 4°C/min. to final temp. 200°C and hold |
| Injection temperature | 250°C |
| Manifold temperature | 250°C |
| Carrier gas | Helium 40 ml/min. |

GC/MS/Computer: A Finnigan 1015 D GC/MS system was used with a data system 6000 series. Its performance has been studied and documented in the same paper as mentioned above. It also includes standard PCB mass spectra and computed reconstructed Aroclor chromatograms. The instrumental data are as follows:

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## Finnigan 1015D GC-MS Instrumental Data

A

Instrumental Data GLC

| | |
|---|---|
| Column | 12' x ¼" all glass |
| Column packing | 6% Apiezon L 80/100 mesh chromosorb W |
| Column temperature | 225°C |
| Injection temperature | 250°C |
| Carrier gas | helium 40 ml/min. |
| Sample size | 5 to 7 microlitres per injection |

B

Instrumental Data Ms

| | |
|---|---|
| Filament current | 100 microamperes |
| Electron energy | 70 or 20 eV |
| Operating pressure | $6.68 \times 10^{-3}$ N/m$^2$ ($5 \times 10^{-6}$ torr) |
| Scanning speed | 4 seconds |
| Standard deviation of spectra | maximum 570 |

After the quadruple MS operating parameters were adjusted the sample was injected into the GC. The ion abundance chromatogram of the GC effluent was acquired by scanning the mass range (40 to 400). The dialogue required for mass spectrometer control, data acquisition and obtaining the plot are given by software programs. At the end of the GC run the computer plots a reconstructed gas chromatogram (ion abundance chromatogram) of total ion amplitude versus the spectrum number. Identification of these chromatographic peaks can be accomplished by plotting the mass spectrum of a specified peak or by a limited mass plot chromatogram which is obtained under computer control by searching through the collected spectra and identifying spectra containing ions with a specific m/e value.

## Result and Discussion

(All chromatograms and computer reconstructed chromatograms are kept on file at the Air Pollution Technology Centre, Department of the Environment, Ottawa, Canada.)

Computer reconstructed gas chromatograms of Aroclor 1242, 1254, and 1260 were made. By focusing on specific mass/charge ratio (m/e) peaks such as 290 (tetra-chloro biphenyls), 324 (penta-chloro) or 358 (hexa-chloro), an ion current plot for a particular PCB isomer versus the Aroclor spectrum is obtained.

Gas chromatograms on Perkin Elmer 990 GC were done for some blank solutions and concentrated samples (all samples were concentrated from about 25 ml to 1 ml). No chlorinated hydrocarbons nor PCB's were found in the samples. If they are present the concentrations are below the sensitivity limit of GC-FID of 1 ng or less.

Mass spectra for the GC peaks of spectrum numbers 365 and 487 from the reconstructed chromatogram plot of sample (WBC-T3, EPA train, Impinger) reveals that only hydrocarbons are present in the sample. No evidence for chlorinated compounds was found. A limit mass searching technique has failed to give any indication of the presence of PCB's. The computer library search of standard Aroclors did not match those obtained from the sample.

It was concluded, therefore, that there were no heavy chlorinated hydrocarbons or PCB's in the samples. If they were present the weights were less than 1 ng.

μσ 1545
SW-147c